



UNIVERSITÉ DE NANTES

INSTITUT DES MATERIAUX JEAN ROUXEL
IMN UMR CNRS 6502 - Université de Nantes



Composés à propriétés électroniques remarquables

Des composés connus
à la recherche de nouveaux composés.

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Plan

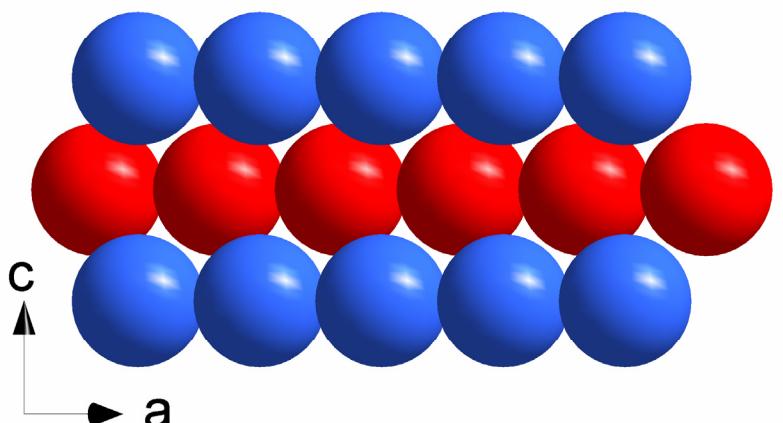
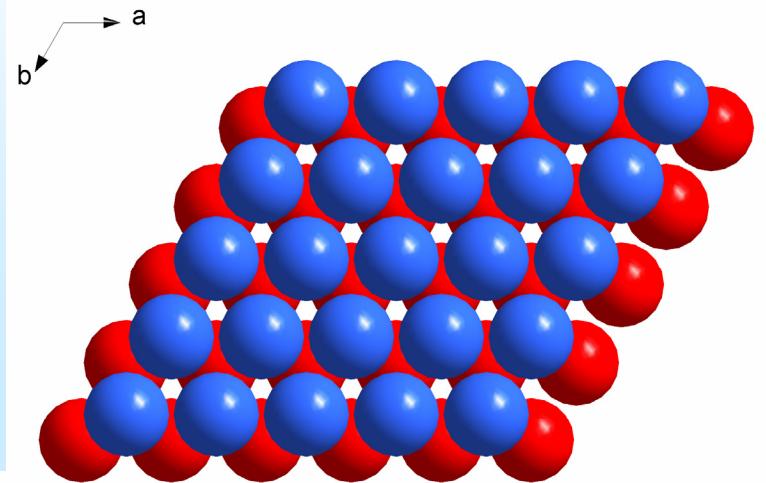
Partie 1 : Structures et propriétés des grandes classes de composés connus

- 1. principaux types structuraux**
- 2. Oxydes de métaux de transition**
- 3. Chalcogénures de métaux de transition**

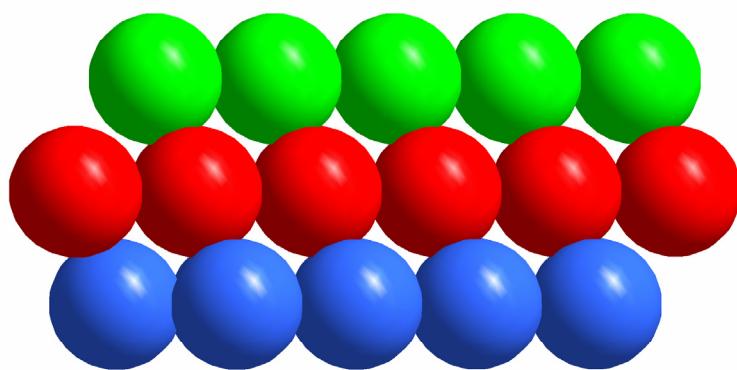
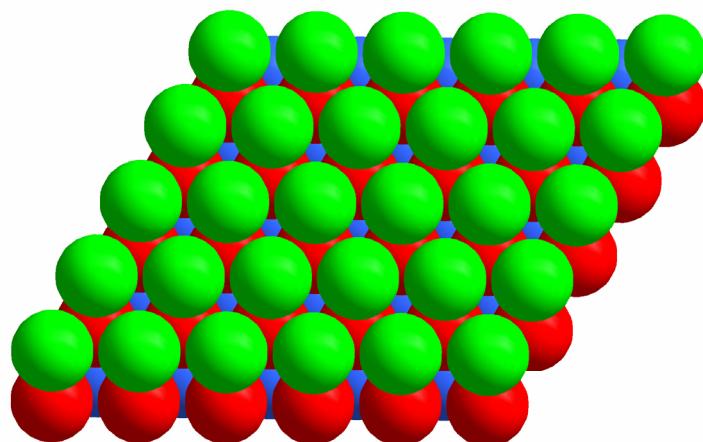
Partie 2 : Recherche de nouveaux composés inorganiques

- 1. Synthèse et recherche exploratoire de nouveaux composés**
- 2. Outils de rationalisation en chimie inorganique**
- 3. Conception raisonnée de nouveaux composés inorganiques**

La nature à horreur du vide : empilements compacts

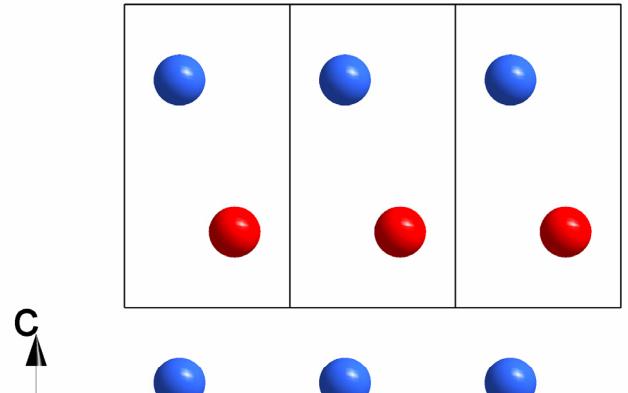


Hexagonal Compact (HC)
ABAB....

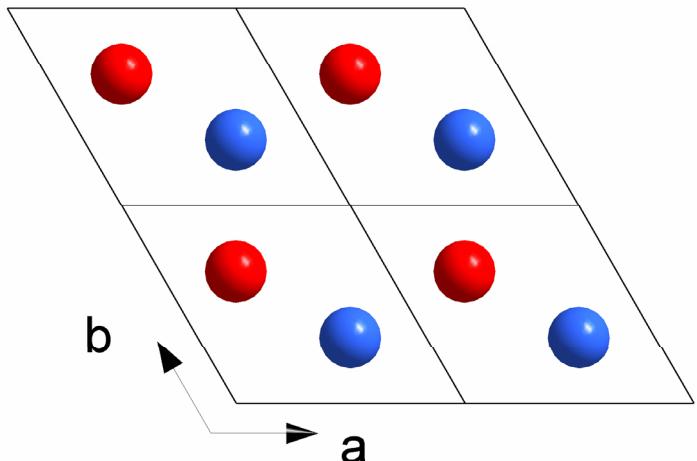


Cubique Faces Centrées (CFC)
ABCABC....

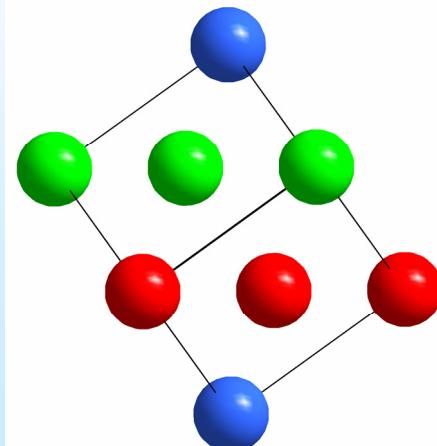
La nature à horreur du vide : empilements compacts



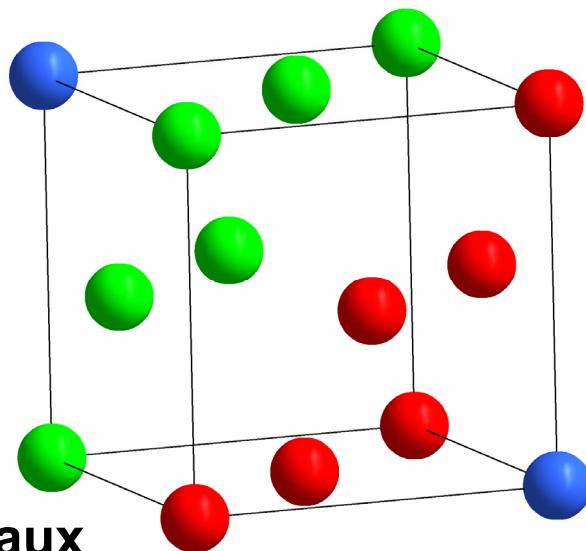
Empilements ABAB =
maille hexagonale



Structure des métaux

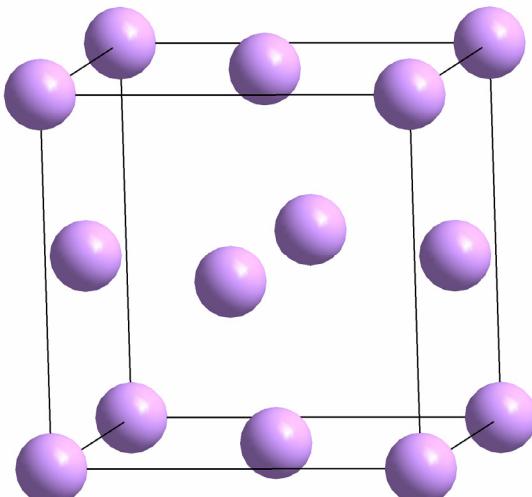
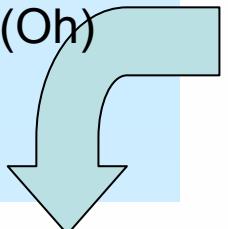


Empilements ABCABC =
maille cubique face centrée



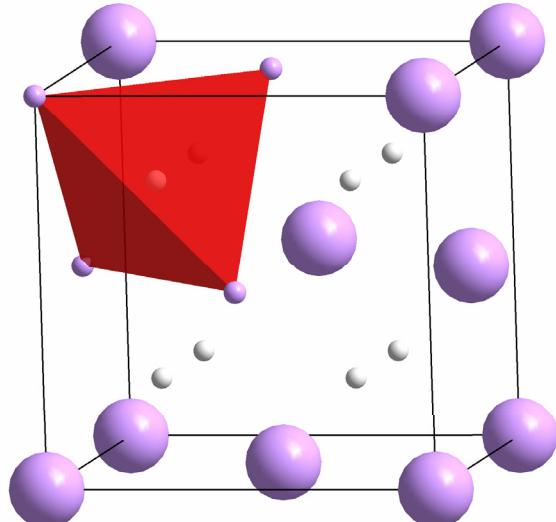
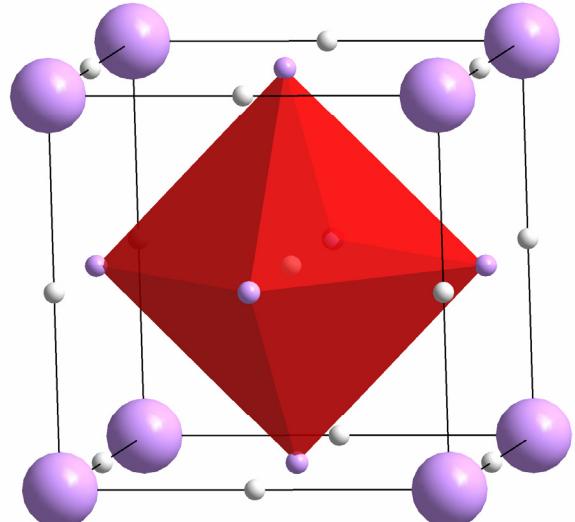
Structures simples : remplissage des empilements CFC et HC

4 sites
octaédriques (Oh)
vides / maille

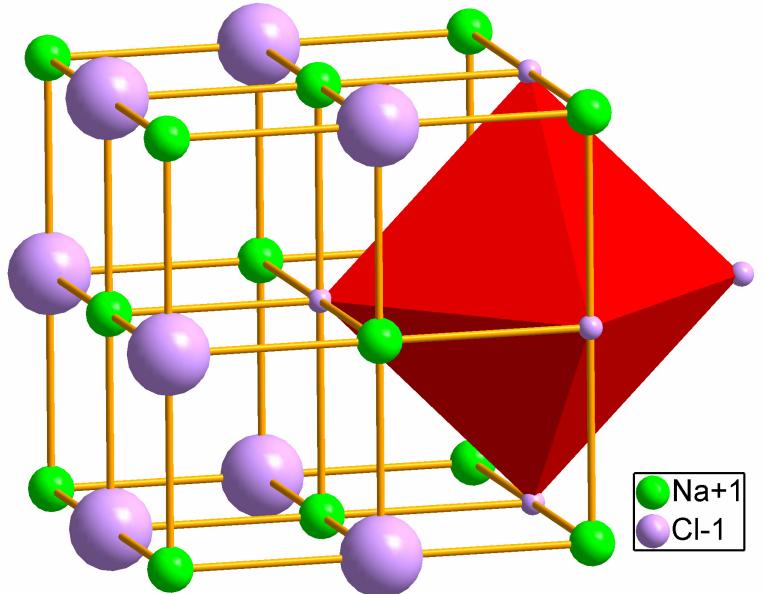


Empilement
Cubique Faces Centrées
CFC 4 atomes / maille

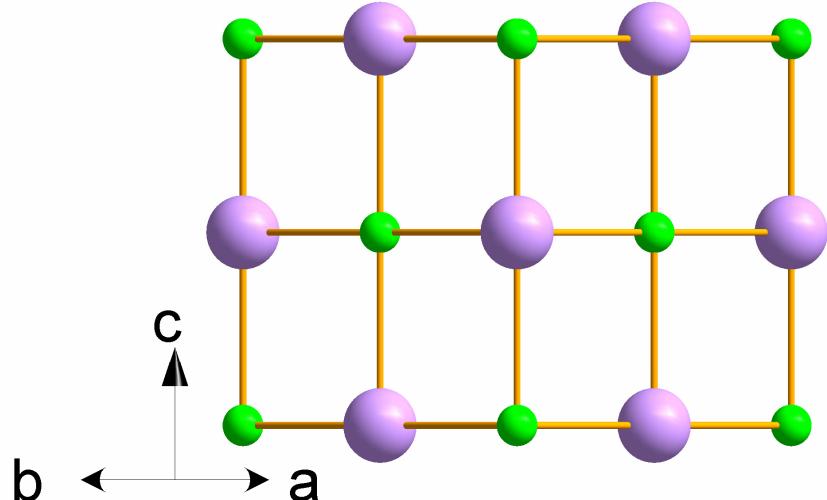
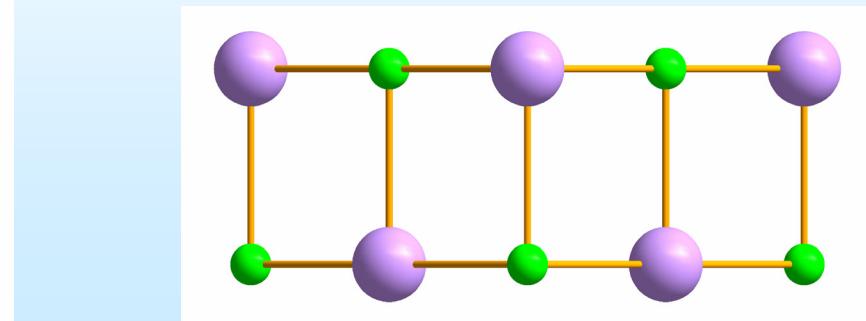
8 sites
tétraédriques (Td)
vides / maille



Structure type NaCl : remplissage de tous les sites octaédriques



Structure des oxydes d'alcalino terreux AeO
 $\text{Ae} = \text{Mg, Ca, Sr, Ba}$
 Des oxydes d'éléments de transition MO
 $\text{M} = \text{Mn, Fe, Co, Ni}$
 Des sulfures de terres rares LnS
 $\text{Ln} = \text{La, Ce ...}$

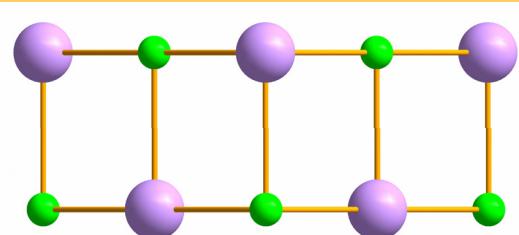


Projection selon 110



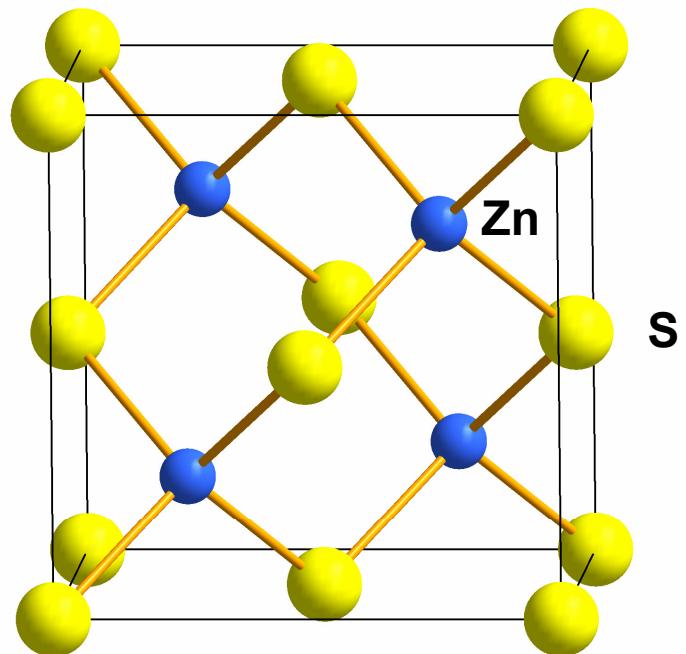
CFC

NaCl

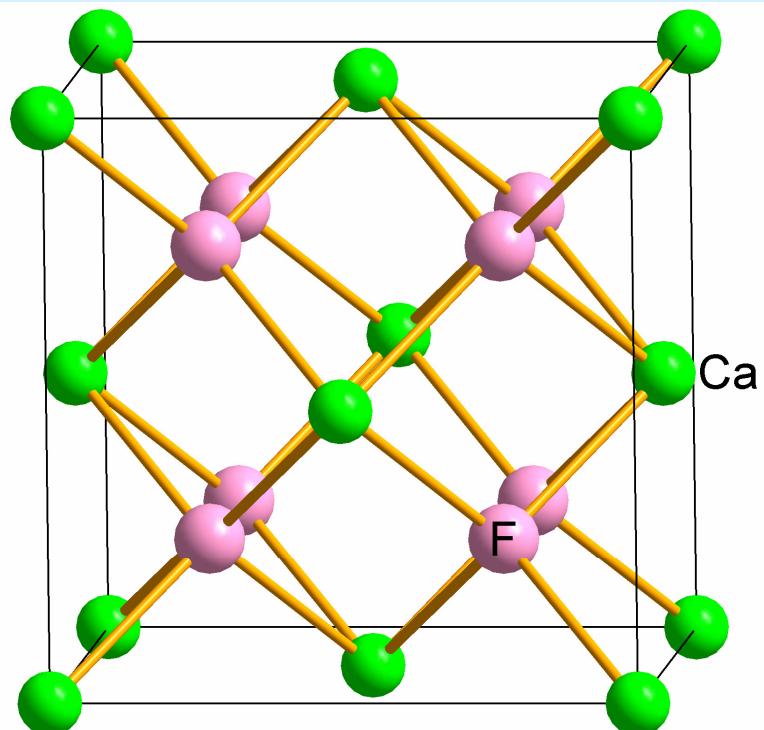


Remplissage des sites Tétraédriques

Un site tétraédrique sur deux :
Structure type ZnS sphalérite

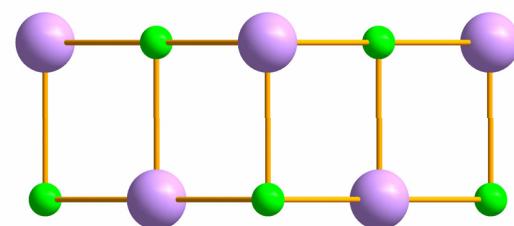


Tous les sites tétraédriques :
Structure type fluorine CaF_2 et
anti fluorine Na_2O

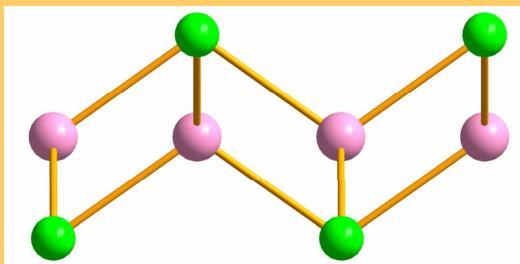




NaCl



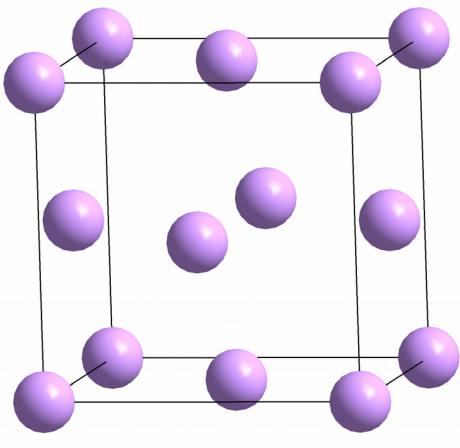
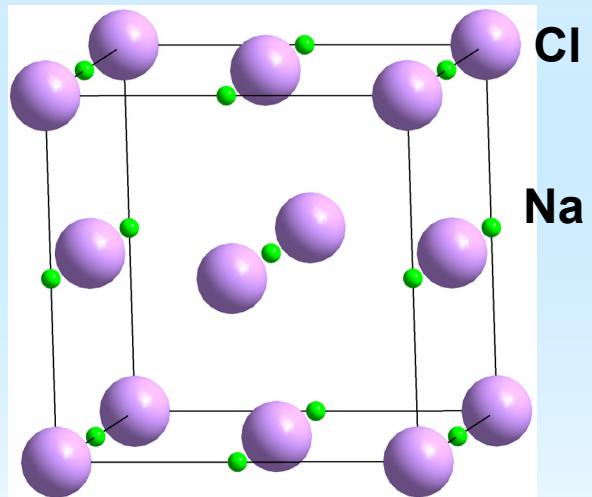
Fluorine



Types structuraux dérivant du CFC

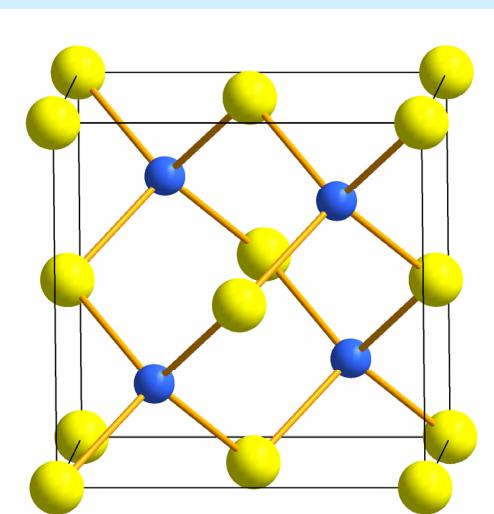
NaCl :

tous les sites Oh

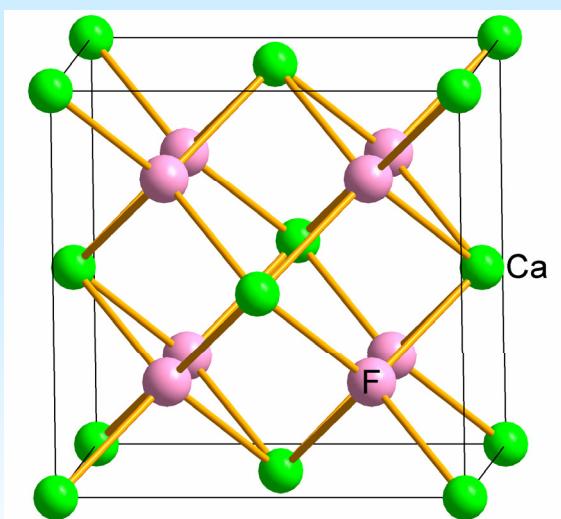


CFC

ZnS :
½ des sites Td

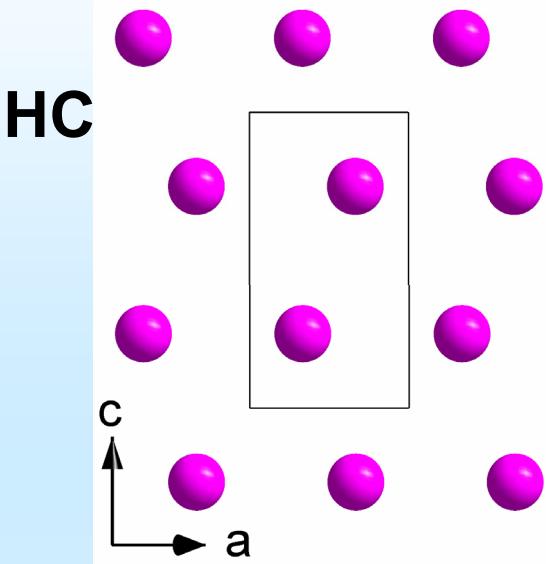
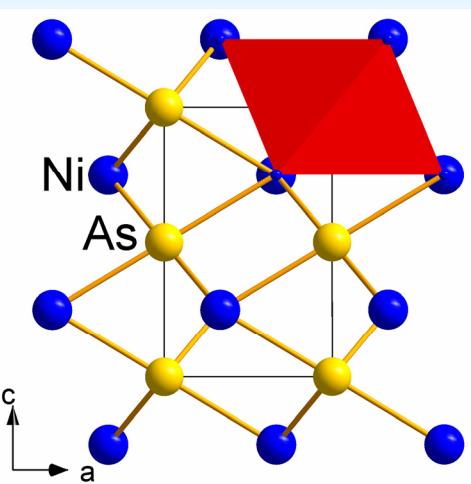


CaF₂ et Na₂O :
tous les sites Td

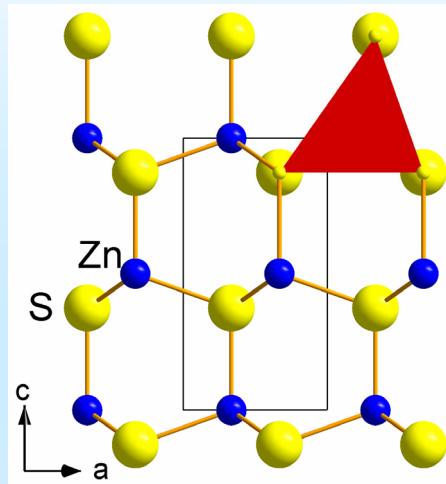


Types structuraux dérivant du HC

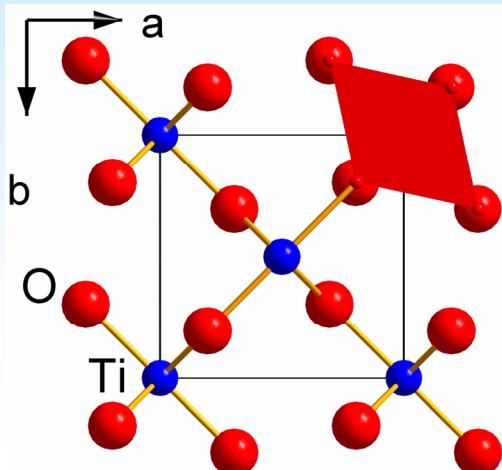
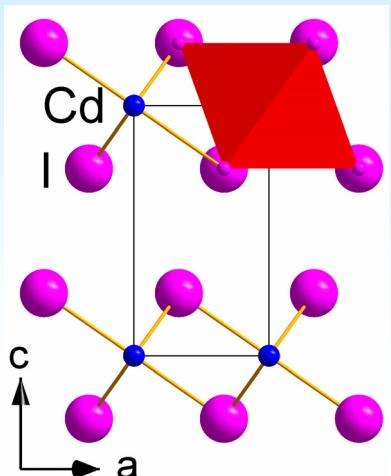
NiAs :
tous les sites Oh



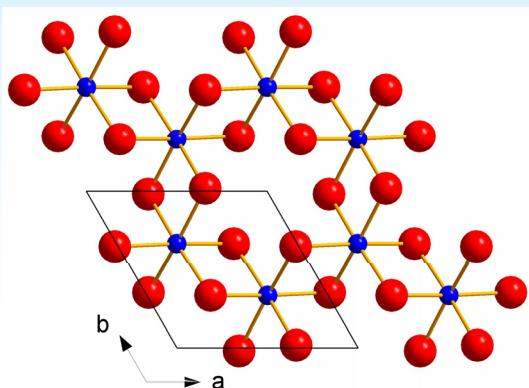
ZnS Wurtzite:
 $\frac{1}{2}$ des sites Td



CdI₂ et TiO₂: $\frac{1}{2}$ des sites Oh



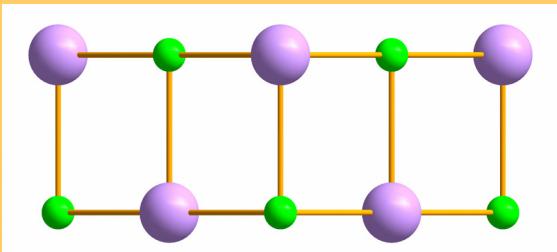
Al₂O₃ Corindon : $\frac{2}{3}$ des sites Oh



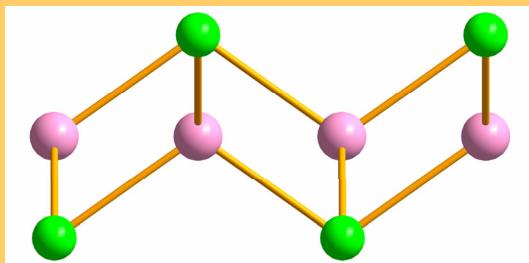


CFC

NaCl

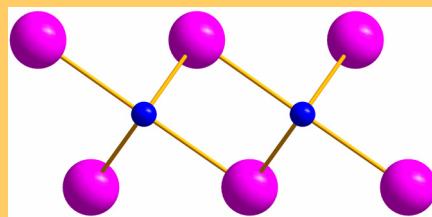


Fluorine



HC

CdI_2



Rationalisation des types structuraux : Degrés d'oxydation et composition

Le degré d'oxydation (D.O.), caractérise l'état électronique d'une espèce chimique par rapport à l'état élémentaire neutre servant de référence (D.O. = 0).

D.O.
+1 +2

hydrogen 1 H 1.0079	
lithium 3 Li 6.941	beryllium 4 Be 9.0122
sodium 11 Na 22.990	magnesium 12 Mg 24.305
potassium 19 K 39.998	calcium 20 Ca 40.078
rubidium 37 Rb 85.468	strontium 38 Sr 87.62
caesium 55 Cs 132.91	barium 56 Ba 137.33
francium 87 Fr [223]	radium 88 Ra [226]

D.O. +2 à +6											
scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	boron 5 B 10.811	carbon 6 C 12.011
yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	aluminum 13 Al 26.982	nitrogen 7 N 14.007
lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.09	gold 79 Au 196.97	mercury 80 Hg 200.59	germanium 31 Ga 69.723	oxygen 8 O 15.999
lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [263]	seaborgium 106 Sg [264]	bohrium 107 Bh [268]	hassium 108 Hs [269]	meitnerium 109 Mt [271]	ununtrium 110 Uun [272]	ununpentium 111 Uuu [277]	ununbium 112 Uub [277]	silicon 14 Si 28.086	fluorine 9 F 18.998
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europlum 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uraniium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]
lutetium 91 Tm 164.93	thulium 92 Yb 173.04	ytterbium 93 No 176.93	erbium 94 Er 176.26	thulium 95 Tm 176.93	ytterbium 96 Yb 176.26	erbium 97 Er 176.93	thulium 98 Tm 176.26	ytterbium 99 Yb 176.93	erbium 100 Er 176.26	thulium 101 Yb 176.26	ytterbium 102 No 176.26
ununquadium 114 Uuq [289]											

* Lanthanide series

** Actinide series

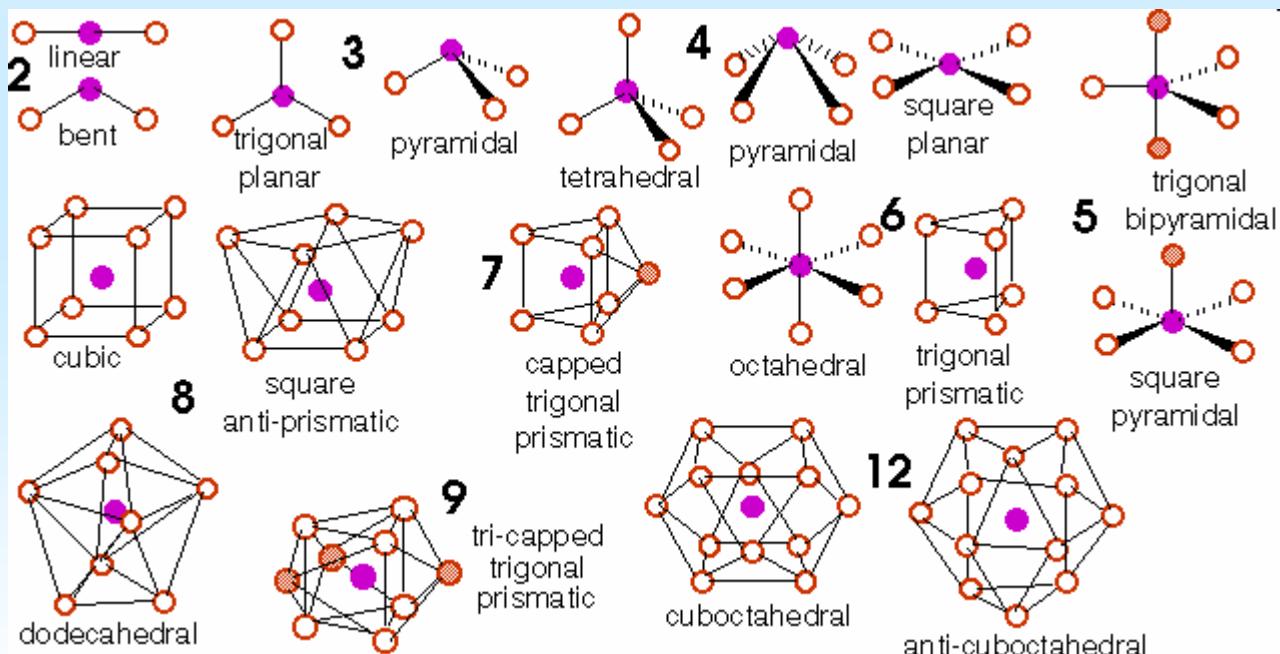
$\text{Ni}^{2+}\text{O}^{2-}$
structure MX 1:1
 NaCl

$\text{Ti}^{4+}(\text{O}^{2-})_2$
structure MX₂ 1:2
Rutile

Pour un composé donné la somme des D.O. est nulle → fixe la composition
→ impact sur la structure

Rationalisation des types structuraux : Rayons ioniques et principaux polyèdres de coordination

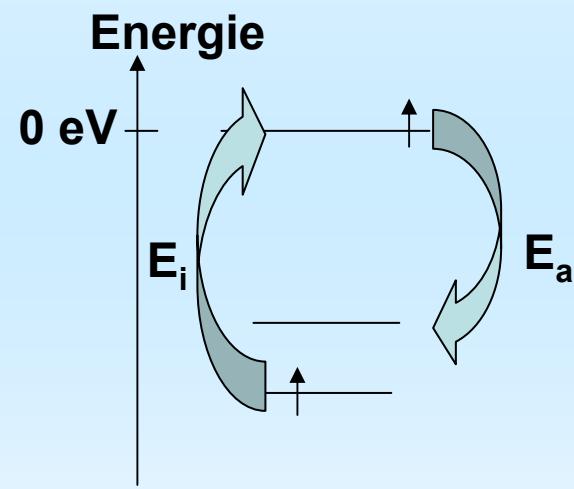
Petits rayons ioniques
Métaux de transition



Gros rayons ioniques
Terres Rares, métaux acalino terreux

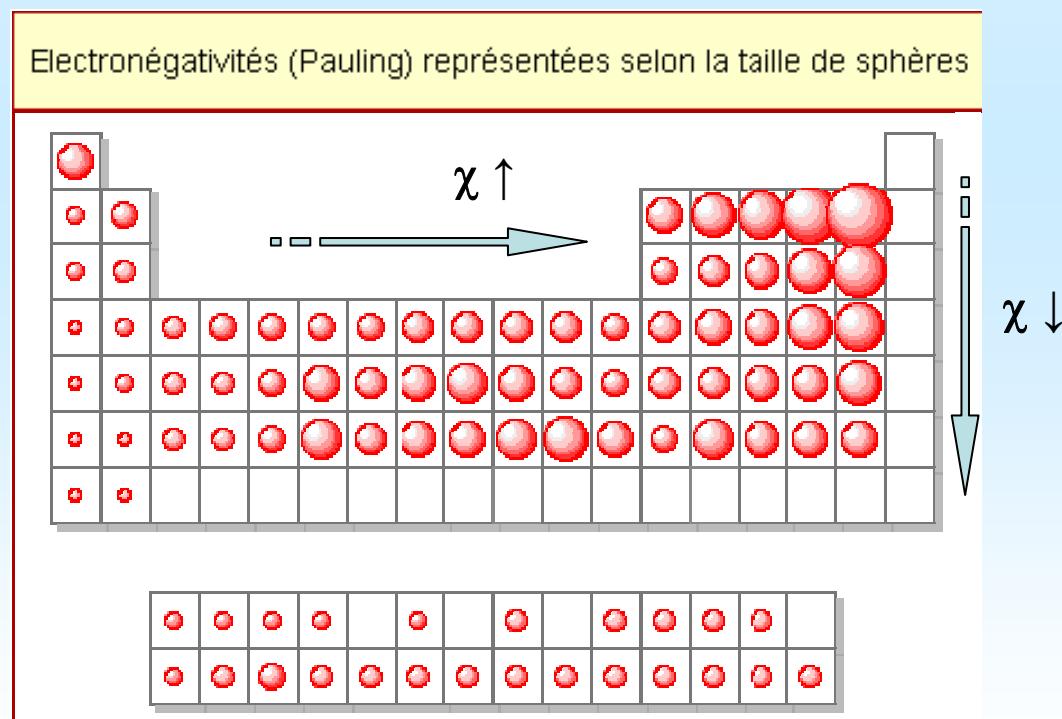
Rationalisation des types structuraux : électronégativité et diagrammes de structure

L'électronégativité est une grandeur relative qui traduit la plus ou moins grande aptitude d'un atome à attirer les électrons de la liaison chimique qui le lie à un autre atome

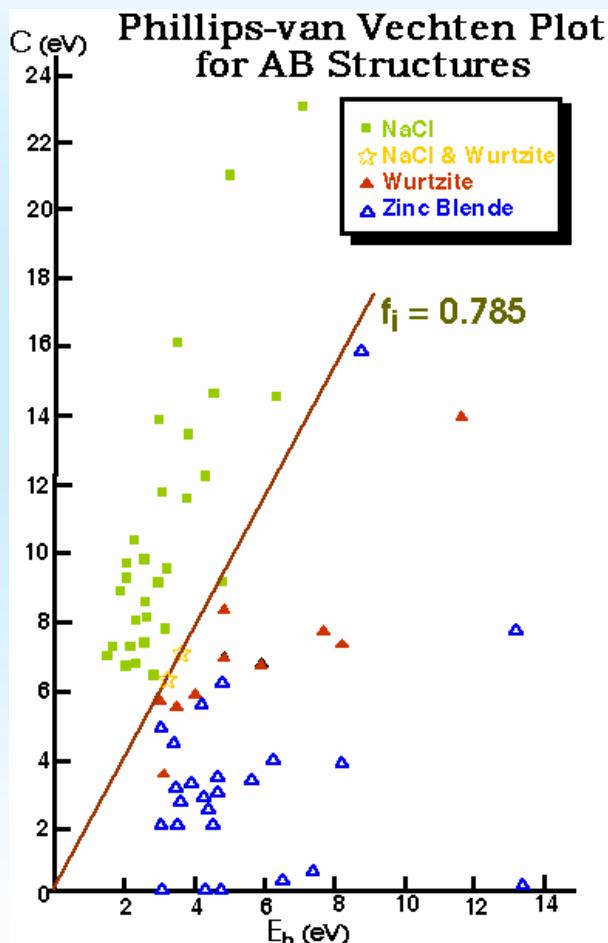
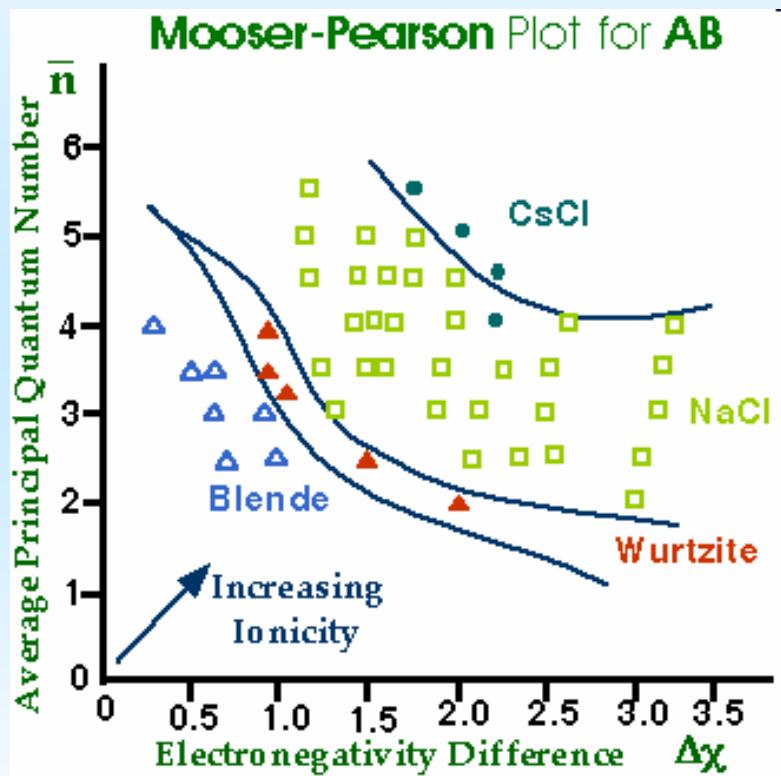


$$\chi(A) = \frac{1}{2} (E_i(A) + E_a(A))$$

Définition de Mulliken



Rationalisation des types structuraux : électronégativité et diagrammes de structure

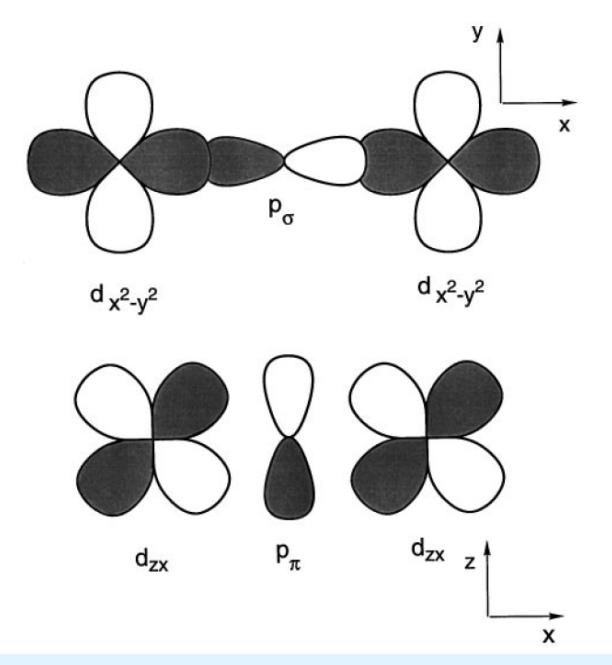


HH et AB
Isoélect.

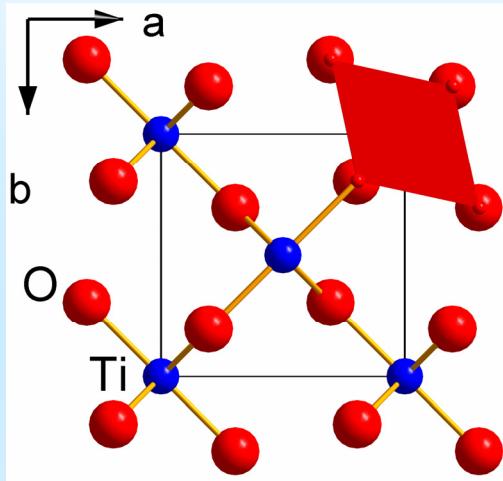
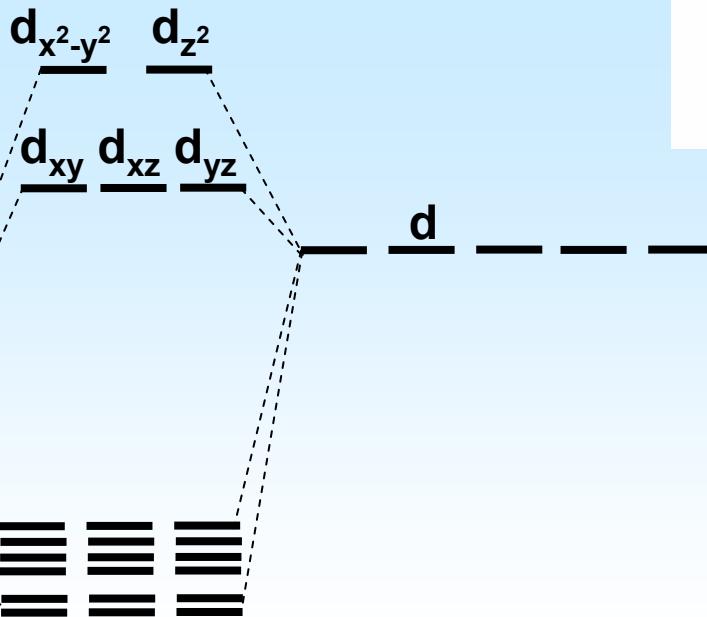
$$E_g(AB) = E_h(HH) + iC$$

Le type structural adopté dépend du rapport des rayons ioniques
et de la différence d'électronégativité

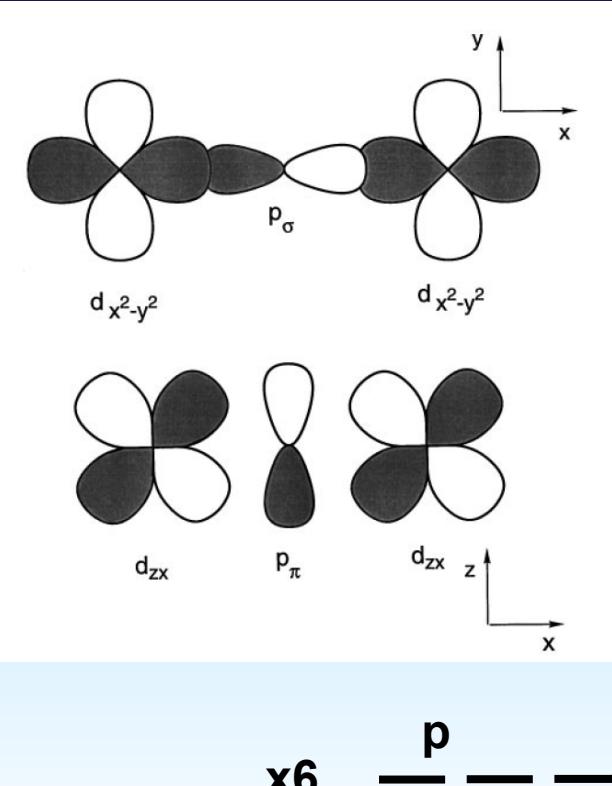
Oxydes binaires : relation structure – structure de bandes - propriétés



TiO₂ Structure Rutile
 $\text{Ti}^{4+}(\text{O}^{2-})_2$ donc d^0



Oxydes binaires : relation structure – structure de bandes - propriétés

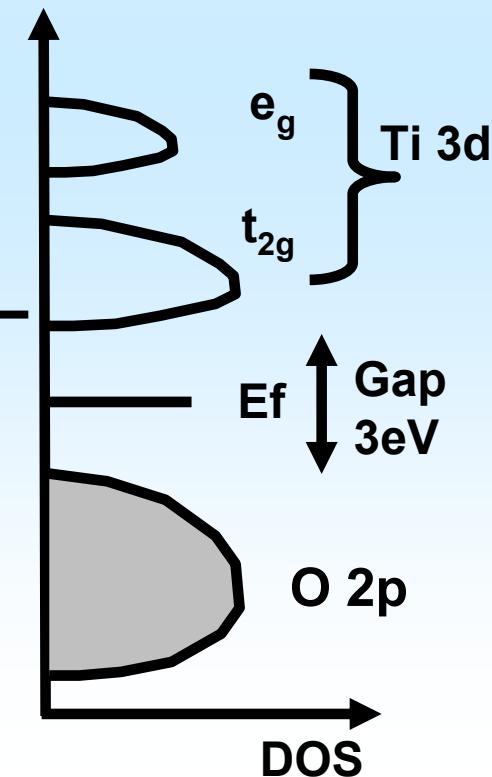


TiO₂ Structure Rutile
 $Ti^{4+}(O^{2-})_2$ donc d^0

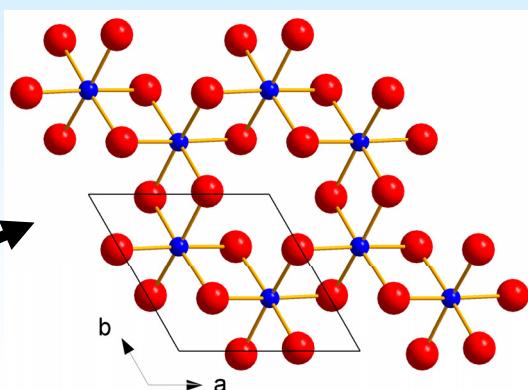
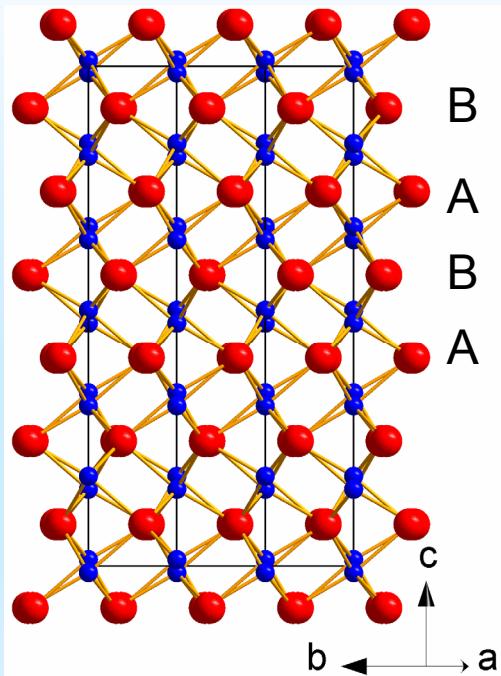
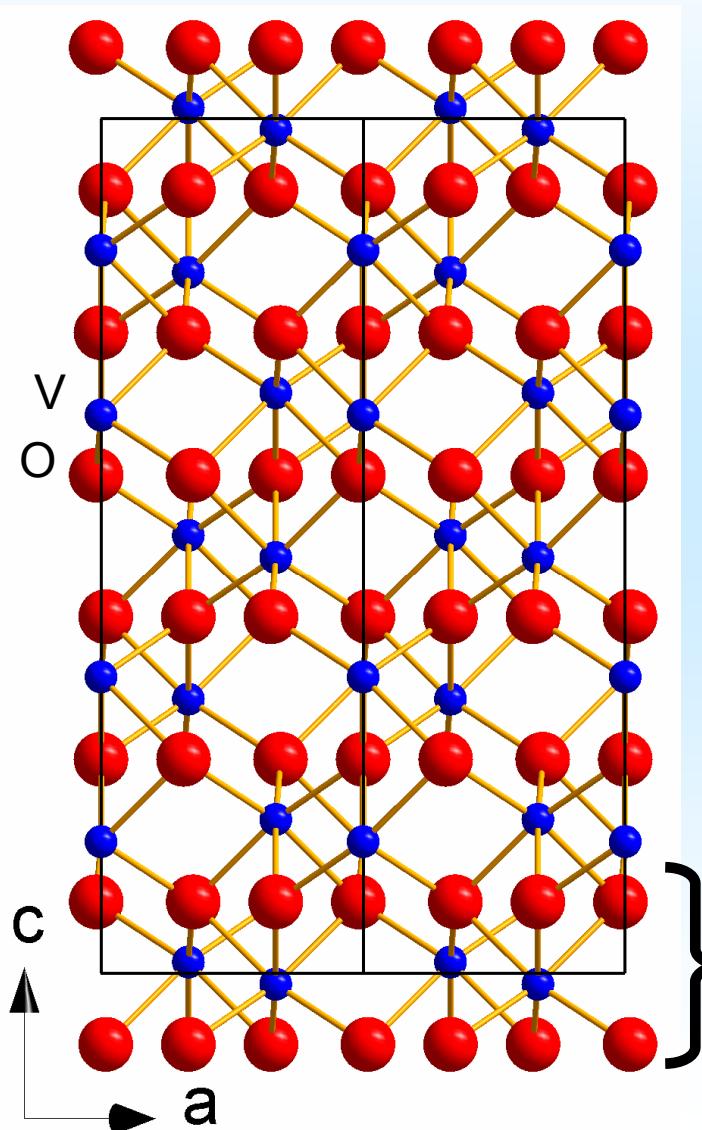
$d_{x^2-y^2}$ d_{z^2}
 d_{xy} d_{xz} d_{yz}



Isolant de bande
Transparent dans le visible
Energie



Les oxydes à structure corindon M_2O_3

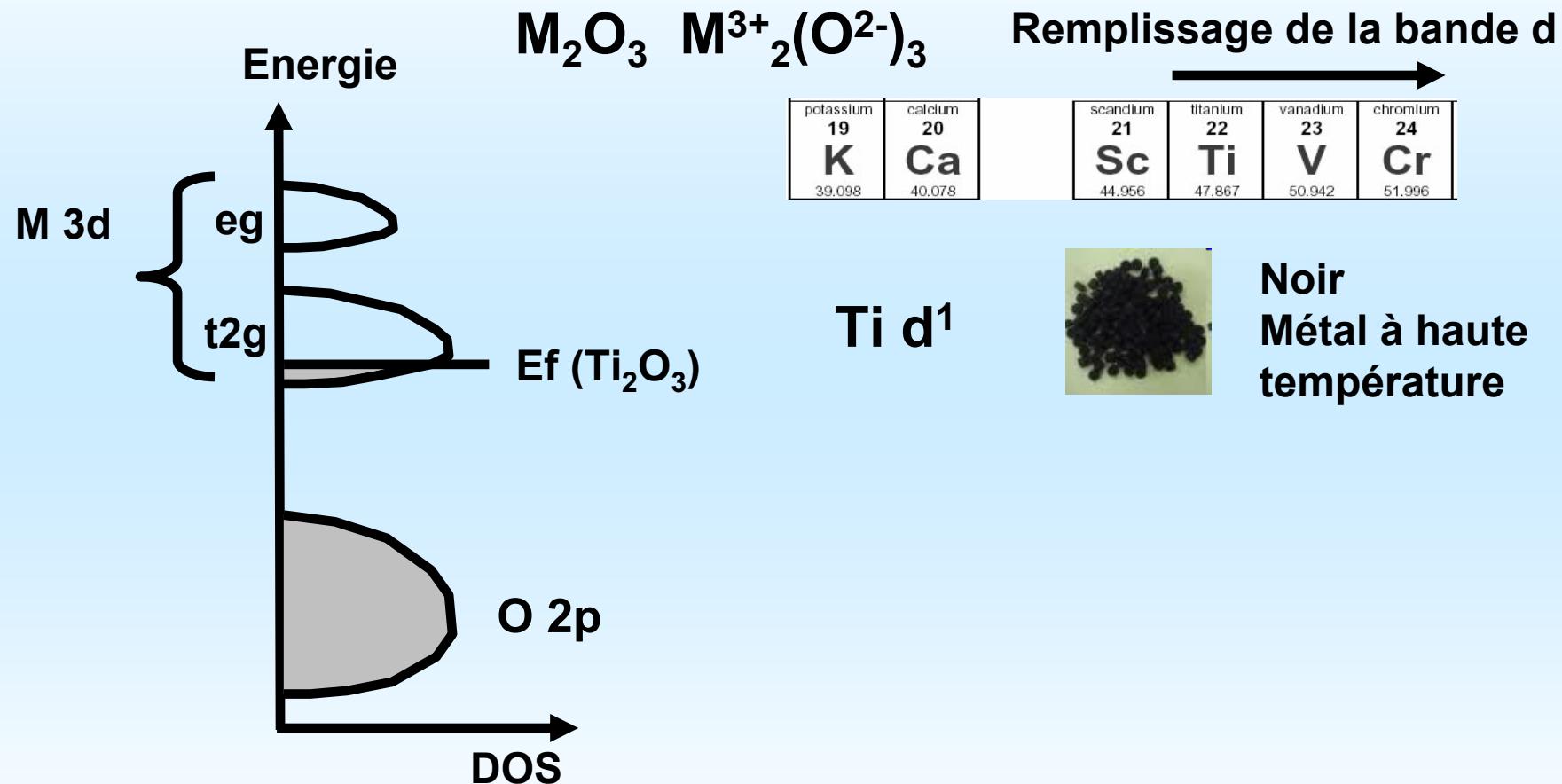


Ti_2O_3
 V_2O_3
 Cr_2O_3

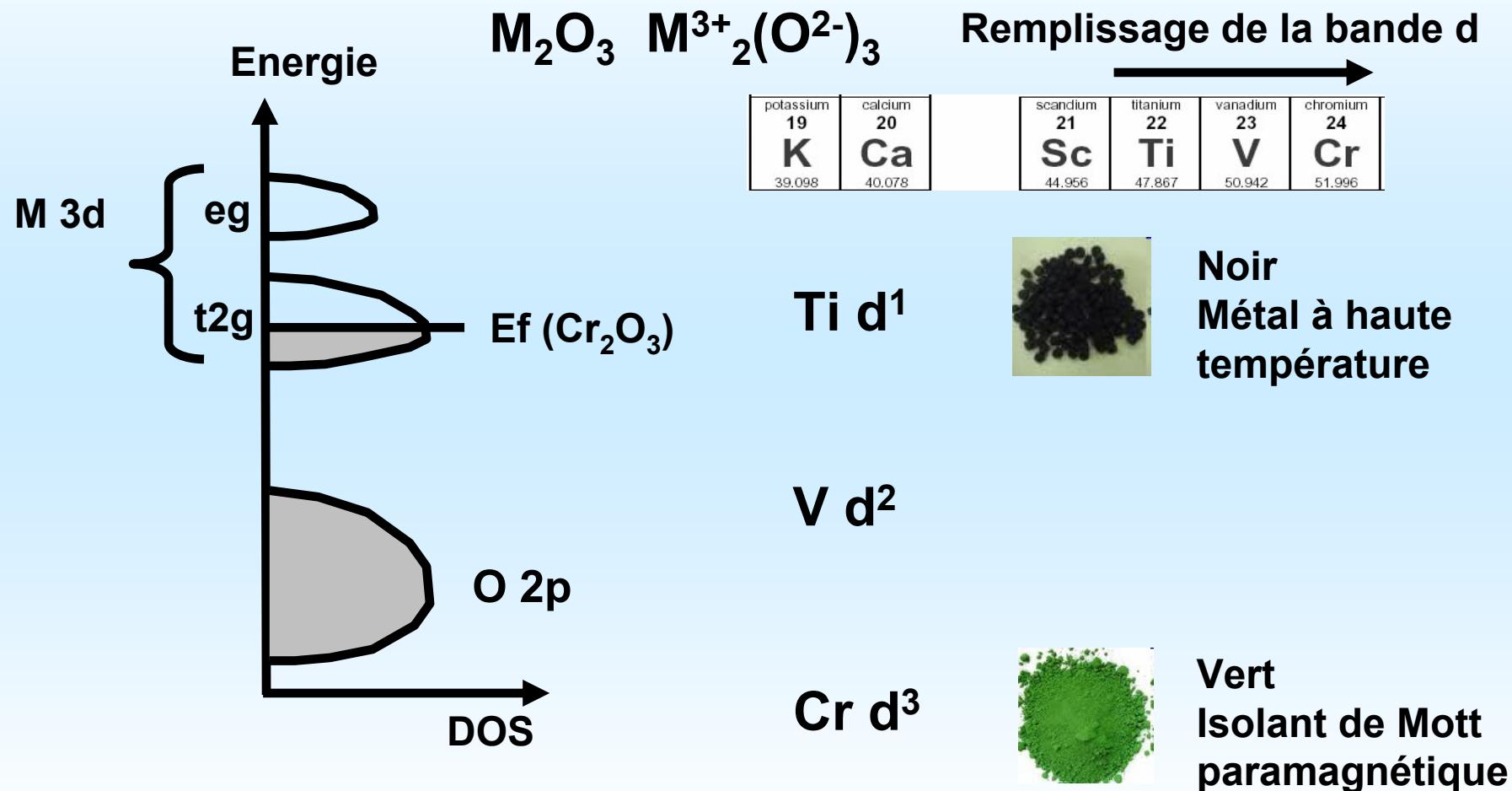
Projection
selon $-2 \bar{1} 0$

Projection
selon $00\bar{1}$

Les oxydes à structure corindon M_2O_3

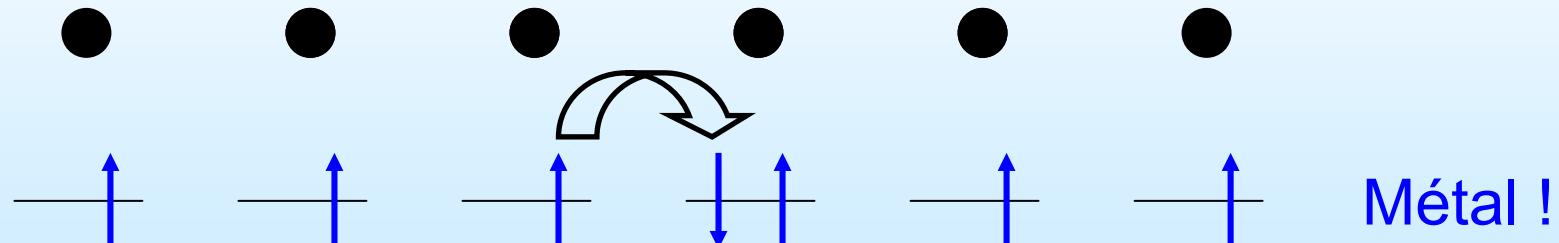


Les oxydes à structure corindon M_2O_3

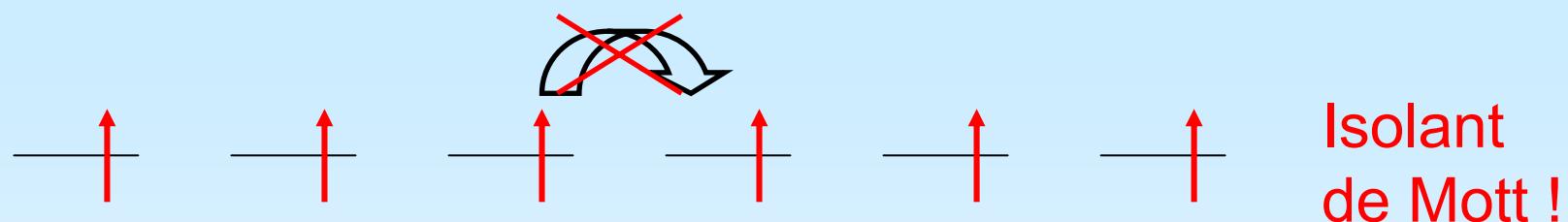


Isolant de Mott : définition

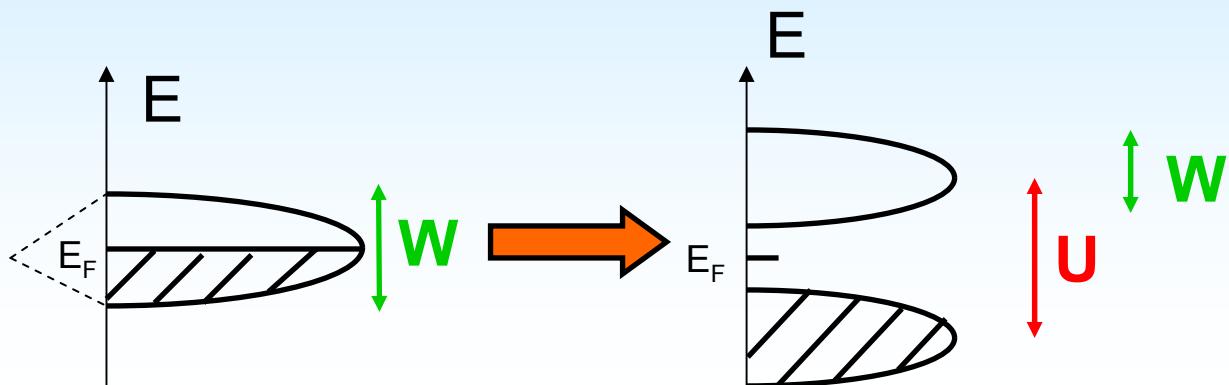
Réseau d'atomes avec une orbitale 1/2 remplie (1 e⁻ par site) :



Si répulsion coulombienne **U** forte entre e⁻ :

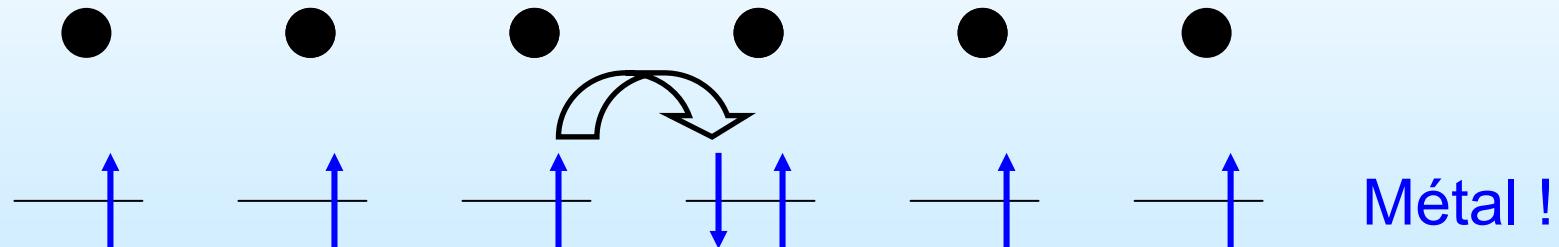


Passage au solide

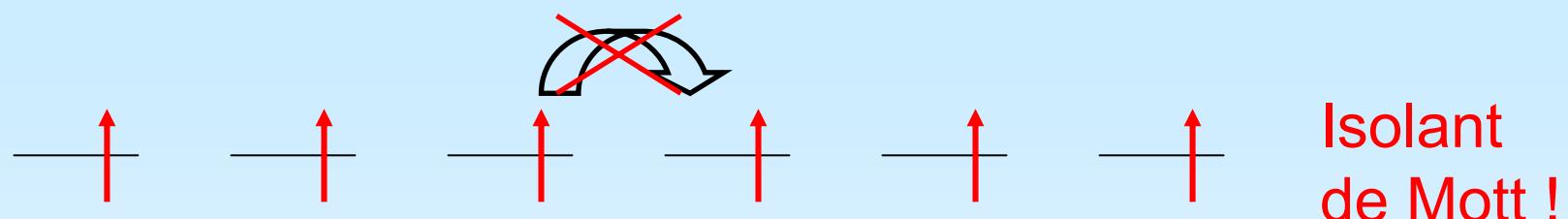


Isolant de Mott : définition

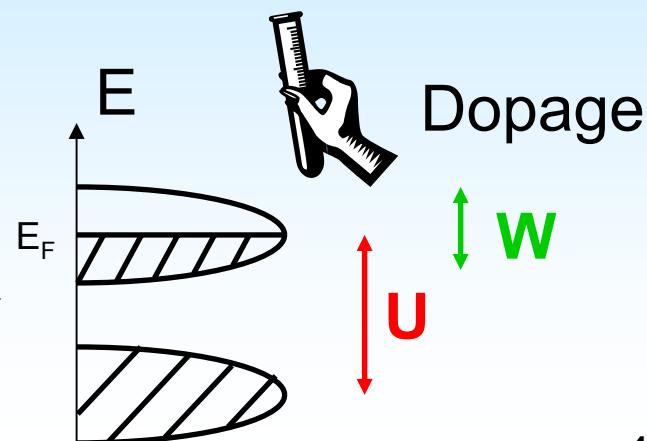
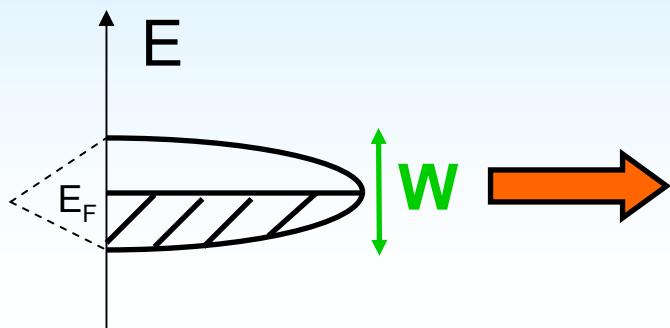
Réseau d'atomes avec une orbitale 1/2 remplie ($1 e^-$ par site) :



Si répulsion coulombienne **U** forte entre e^- :

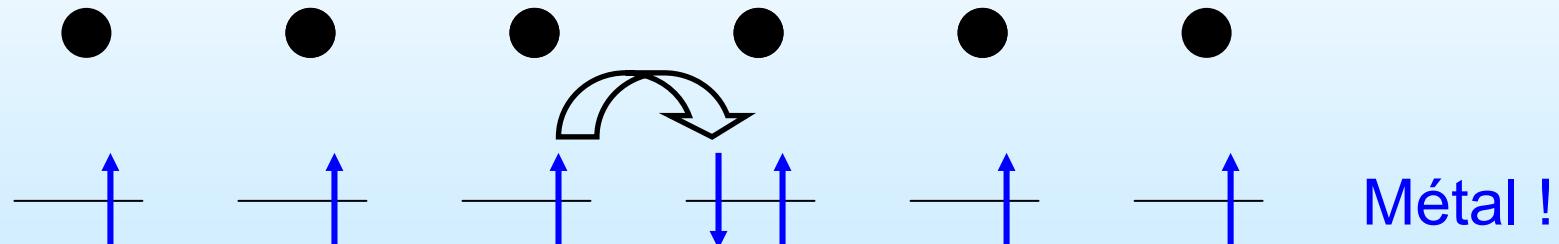


Passage au solide

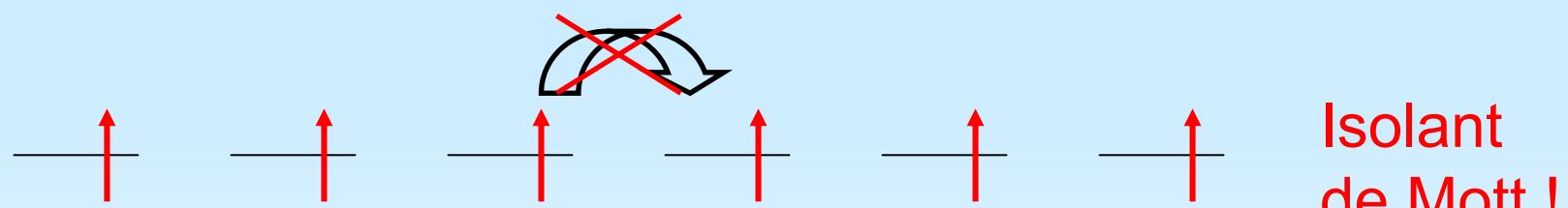


Isolant de Mott : définition

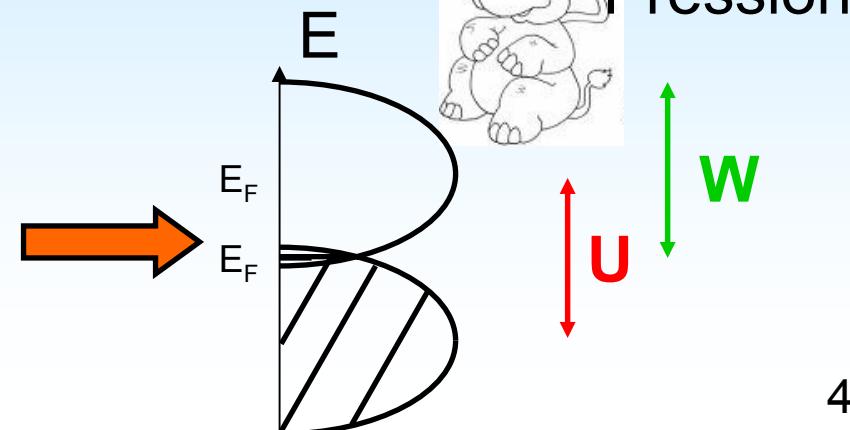
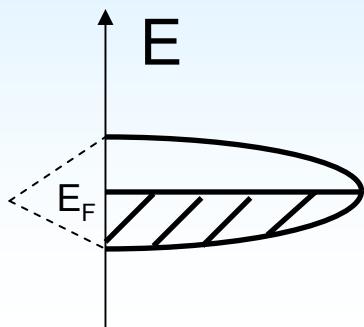
Réseau d'atomes avec une orbitale 1/2 remplie (1 e⁻ par site) :



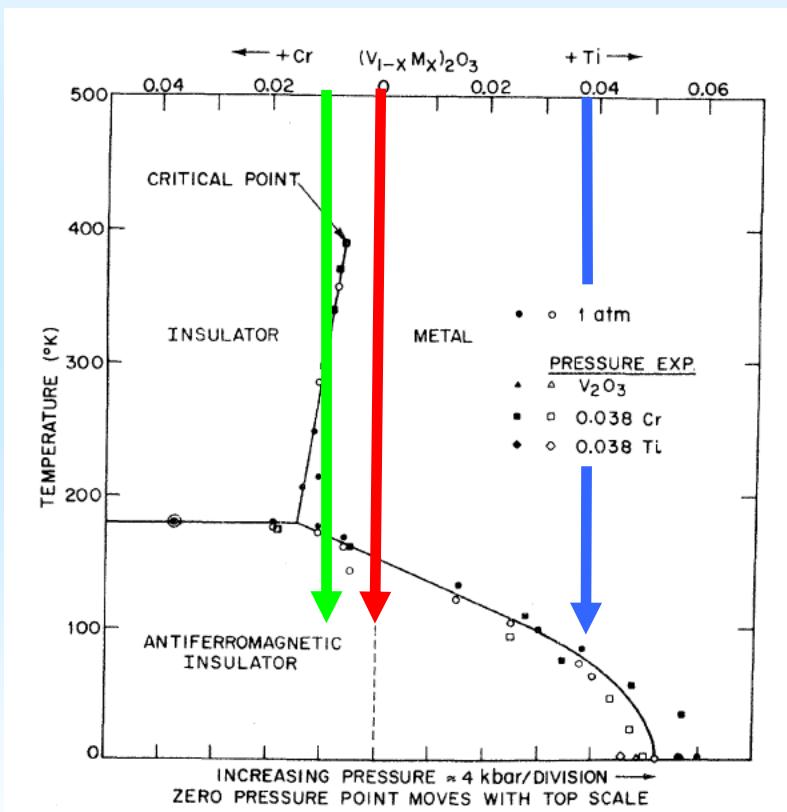
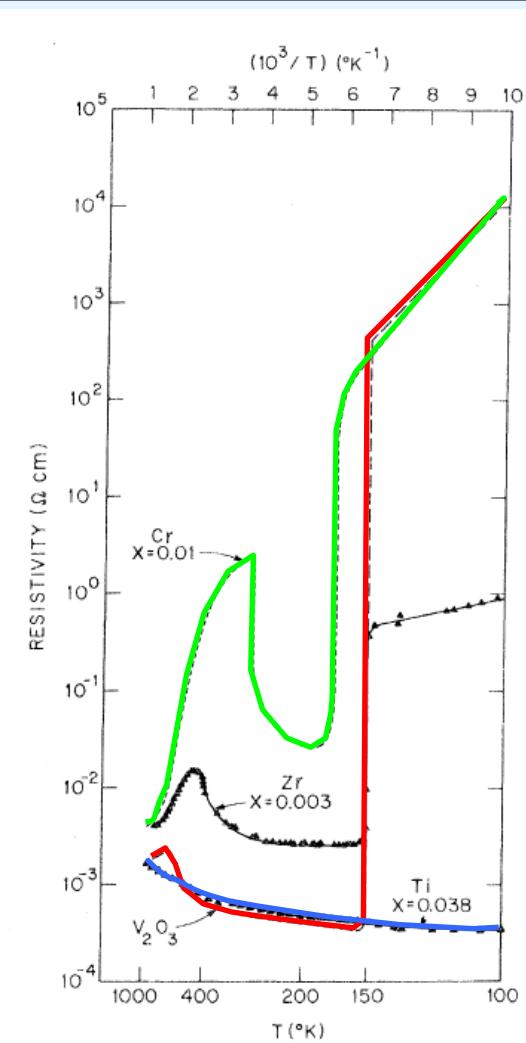
Si répulsion coulombienne **U** forte entre e⁻ :



Passage au solide



V_2O_3 transition isolant métal pilotée par la largeur de bande ou par changement structural



PHYSICAL REVIEW B

VOLUME 7, NUMBER 5

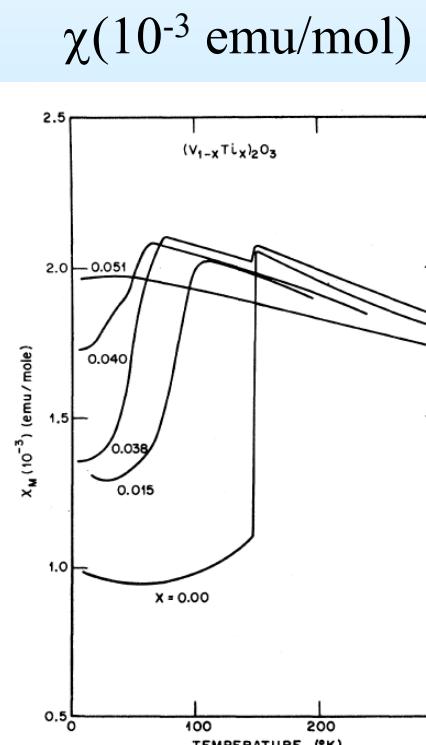
T(K)

Metal-Insulator Transitions in Pure and Doped V_2O_3

D. B. McWhan, A. Menth*, J. P. Remeika, W. F. Brinkman, and T. M. Rice

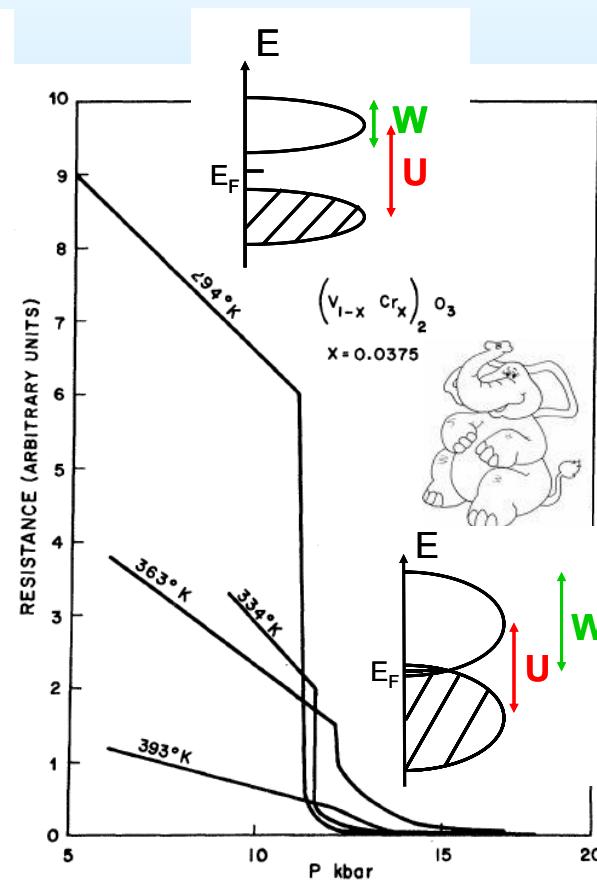
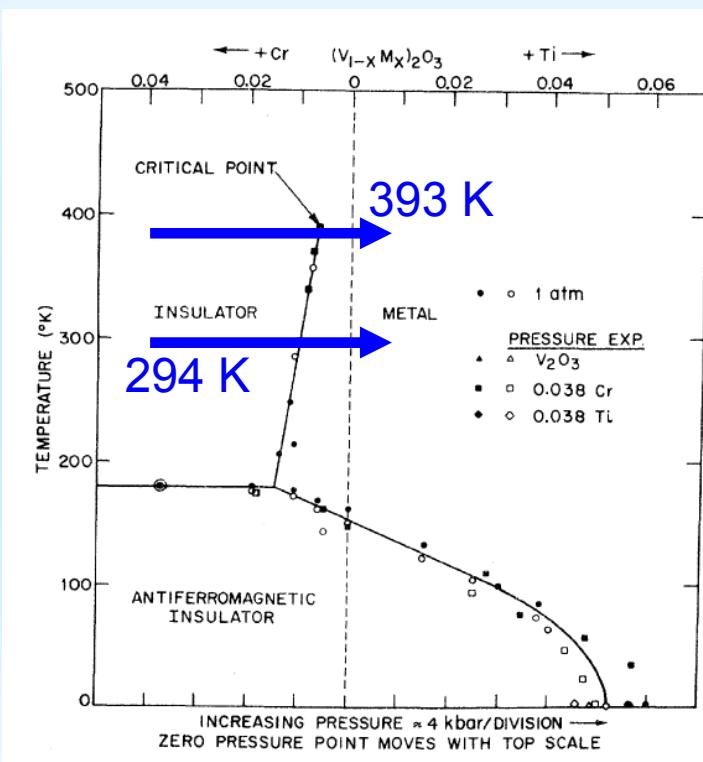
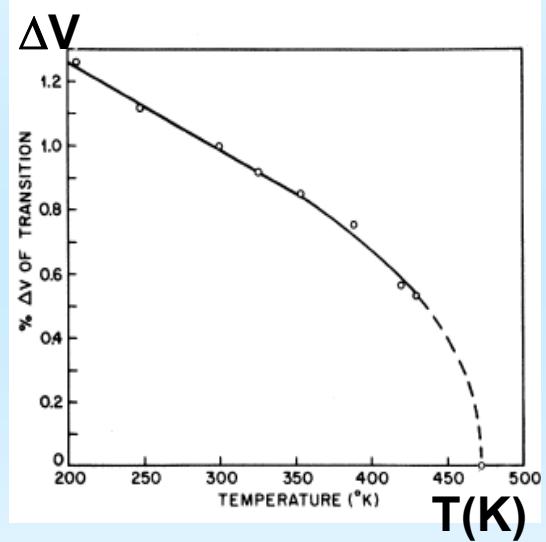
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 31 January 1972)



1 MARCH 1973

V_2O_3 transition isolant métal pilotée par largeur de bande



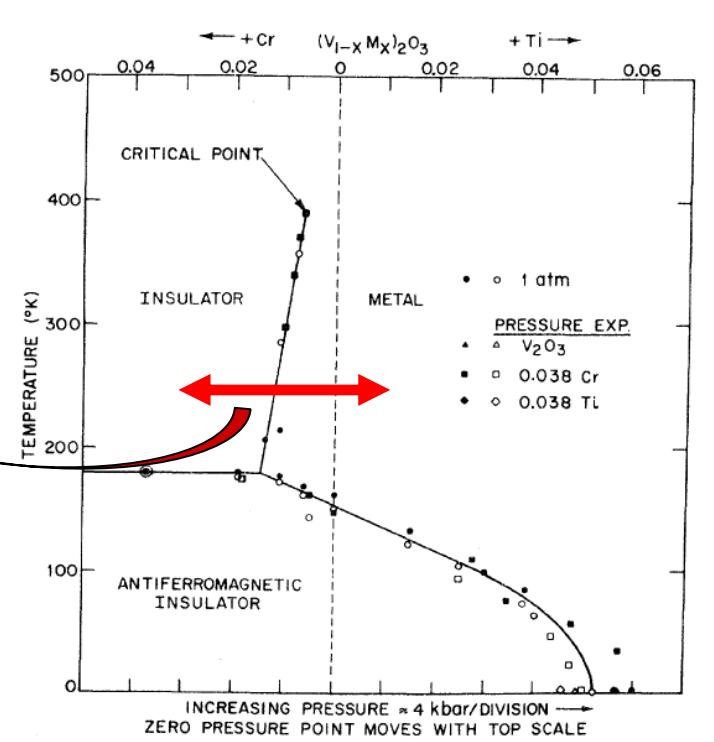
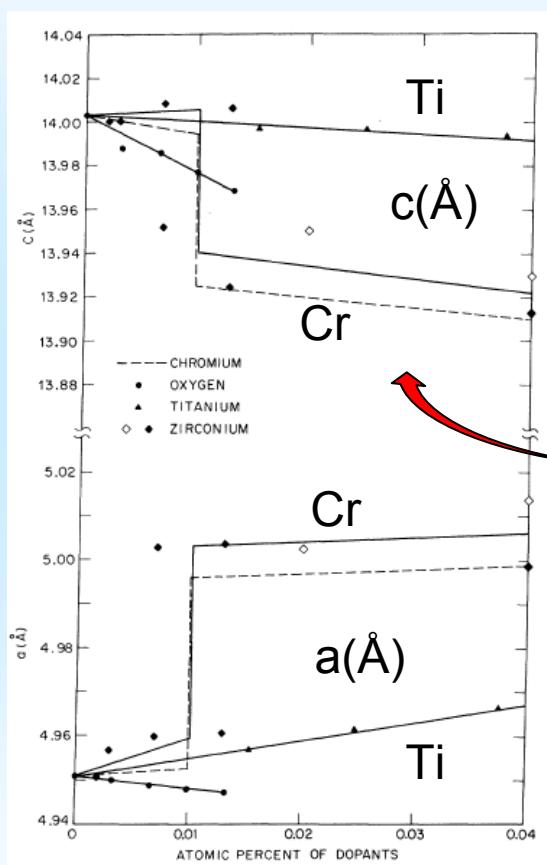
Metal-Insulator Transitions in Pure and Doped V_2O_3

D. B. McWhan, A. Menth*, J. P. Remeika, W. F. Brinkman, and T. M. Rice

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 31 January 1972)

V_2O_3 transition isolant métal pilotée par la largeur de bande



Rayon ionique \downarrow

titanium	22	vanadium	23	chromium	24
Ti	47.867	V	50.942	Cr	51.996

Pression chimique
=
Pression physique



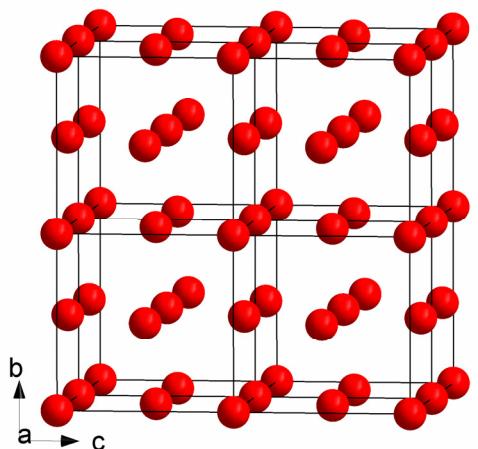
Metal-Insulator Transitions in Pure and Doped V_2O_3

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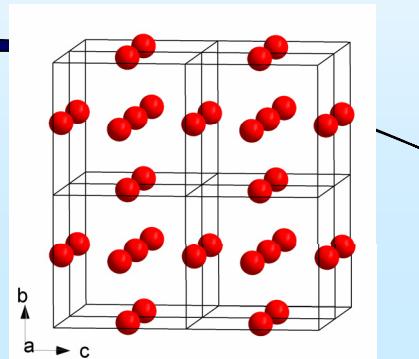
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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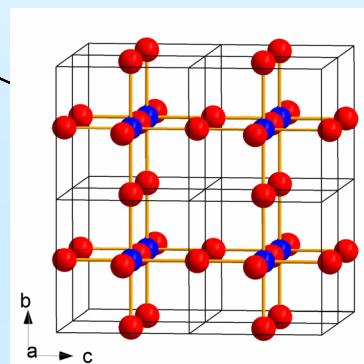
Oxydes mixtes ABO_3 à structure pérovskite



Suppression
 $\frac{1}{4}$ O (sommet)



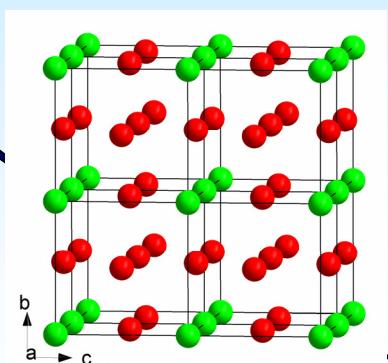
Remplissage
 $\frac{1}{4}$ site Oh



Type
 ReO_3

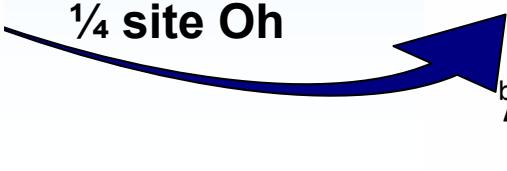
Remplissage
site cubique

remplacement
 $\frac{1}{4}$ O par A

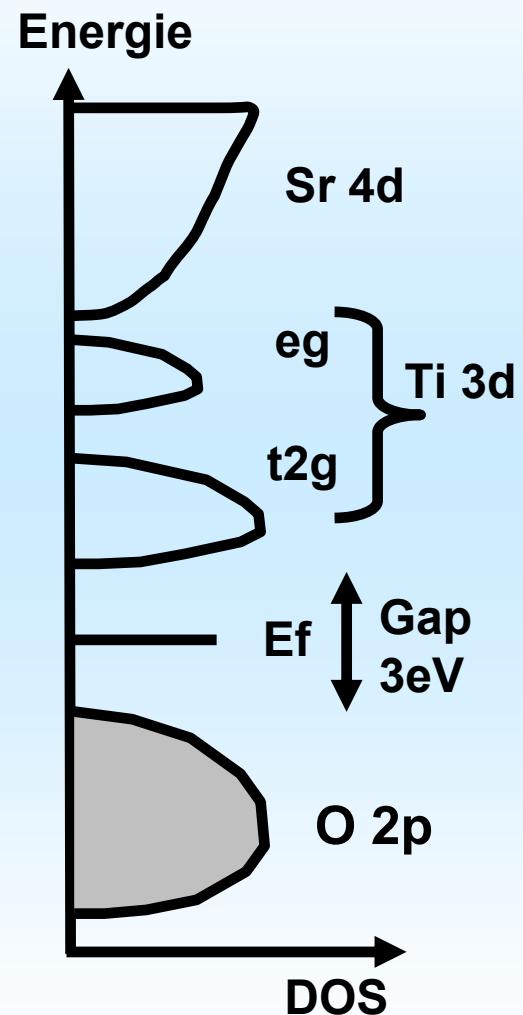
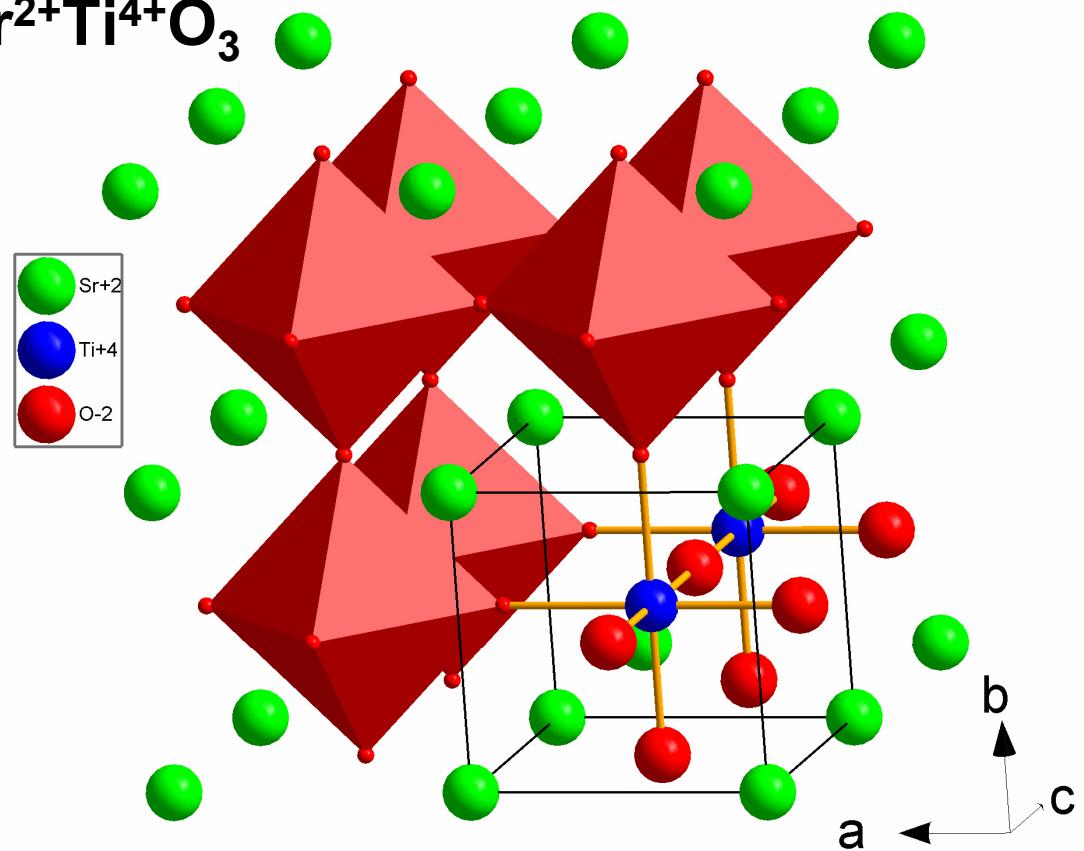


Pérovskite
 ABO_3

Remplissage
 $\frac{1}{4}$ site Oh



Oxydes mixtes ABO_3 à structure pérovskite

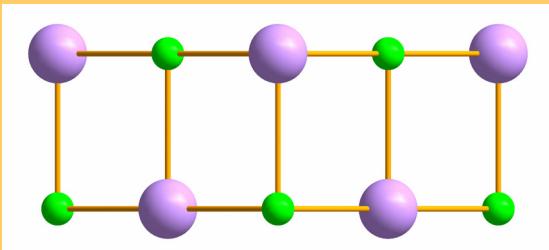


Structure de beaucoup d'oxydes mixtes avec
A = alcalino terreux ou terres rares
B = éléments de transition

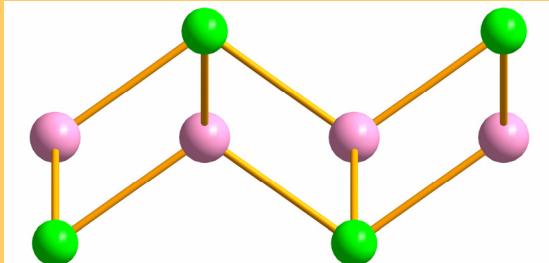
Isolant de bande



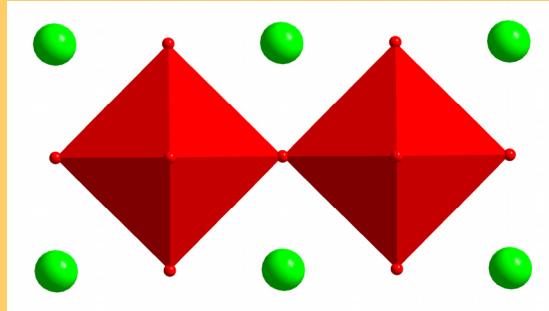
NaCl



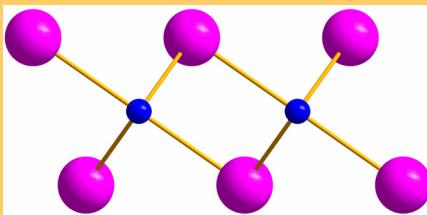
Fluorine



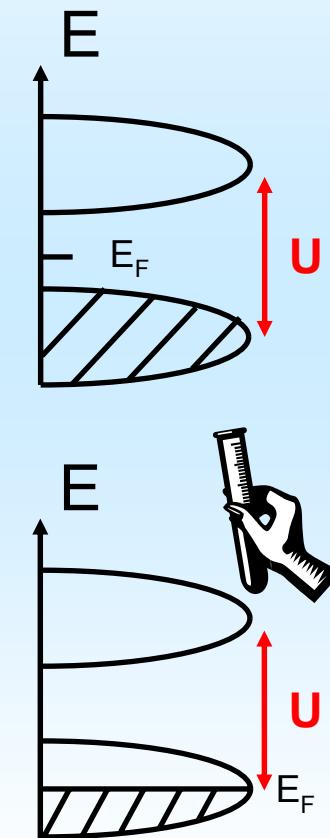
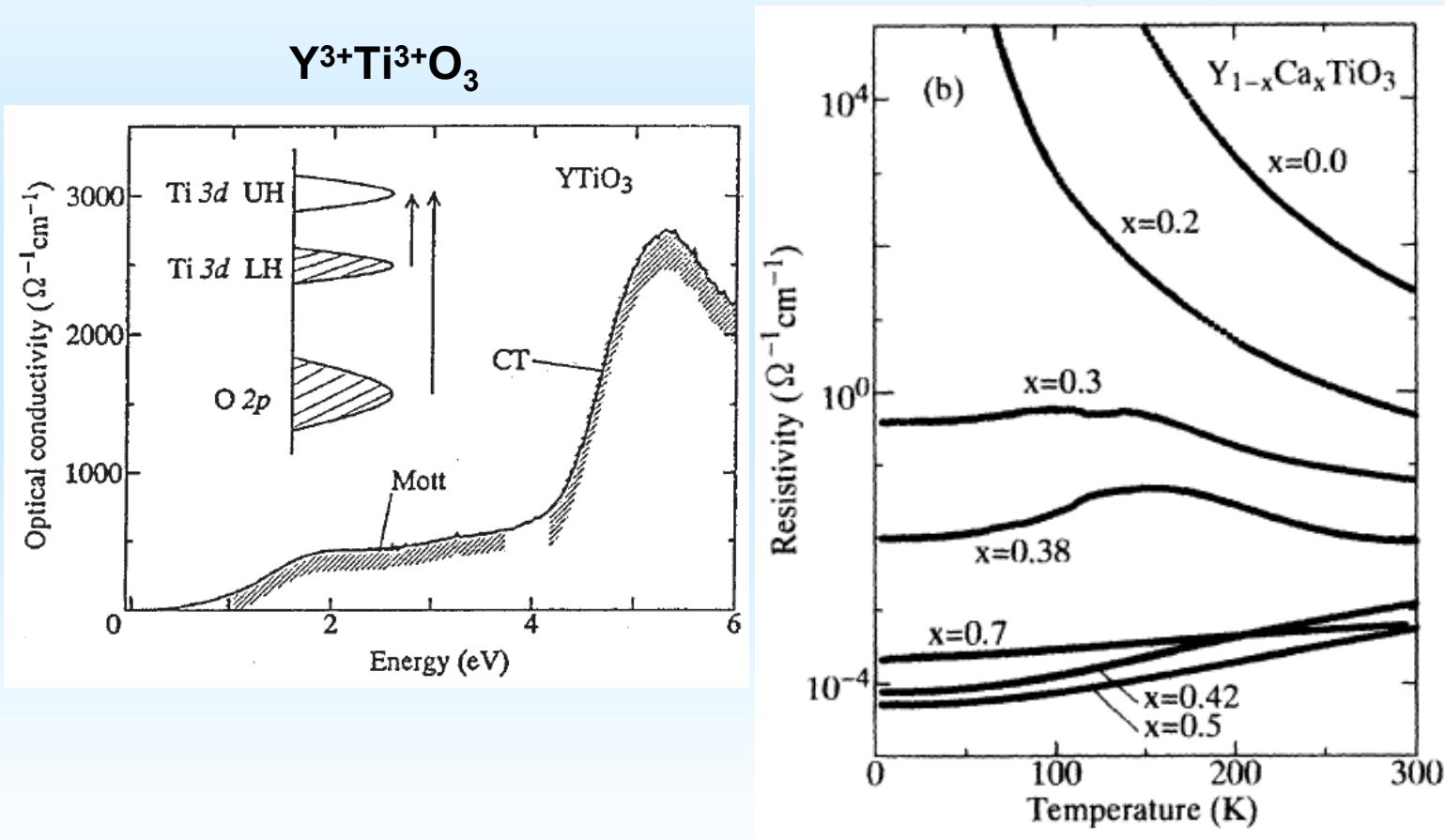
Perovskite



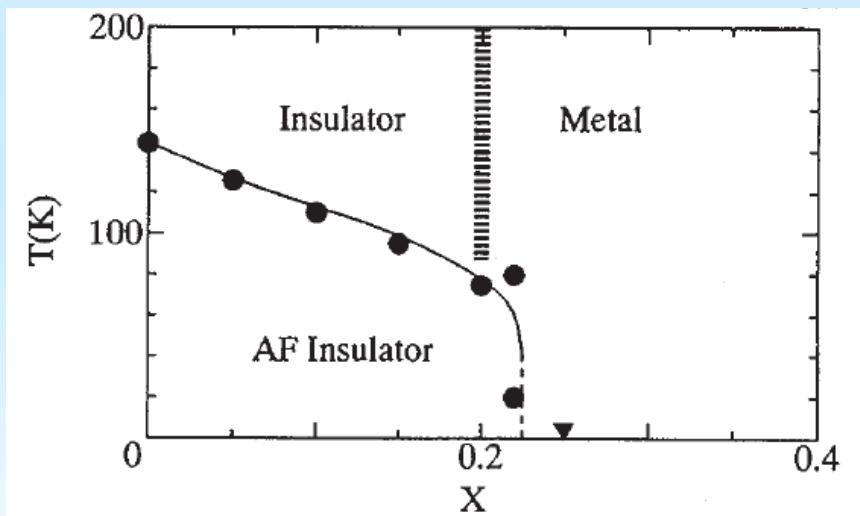
CdI₂



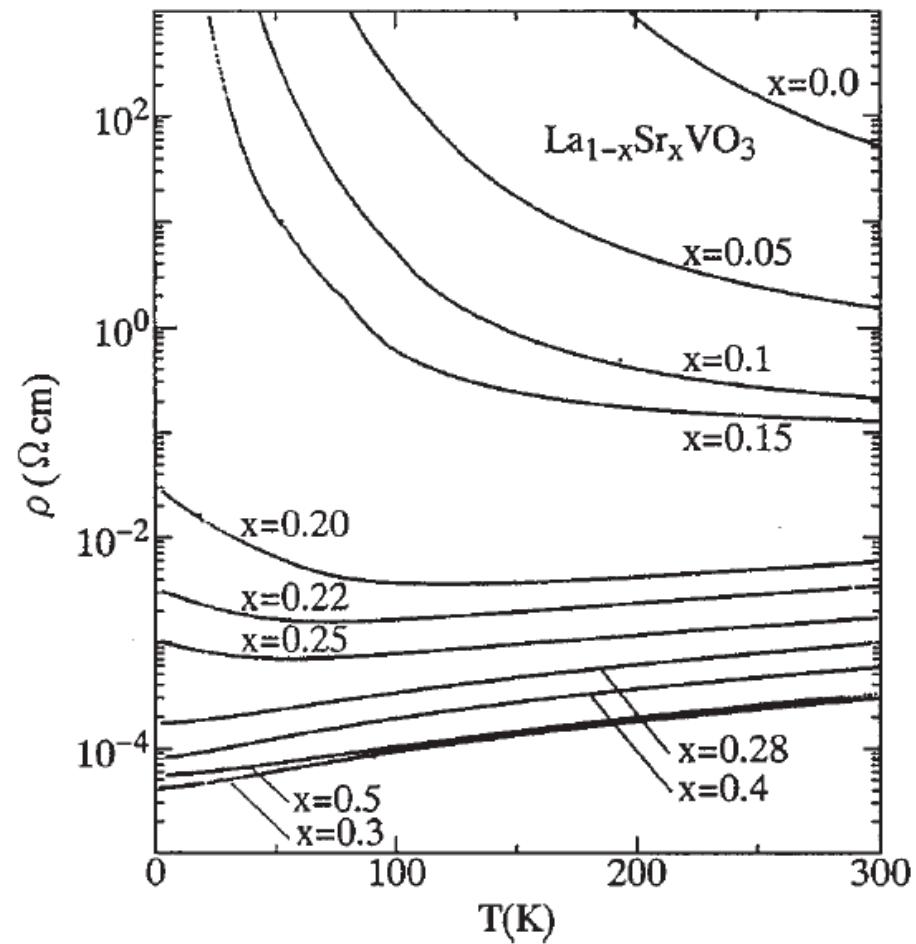
Transition Isolant métal contrôlée par le remplissage dans la série $Y_{1-x}Ca_xTiO_3$ à structure pérovskite



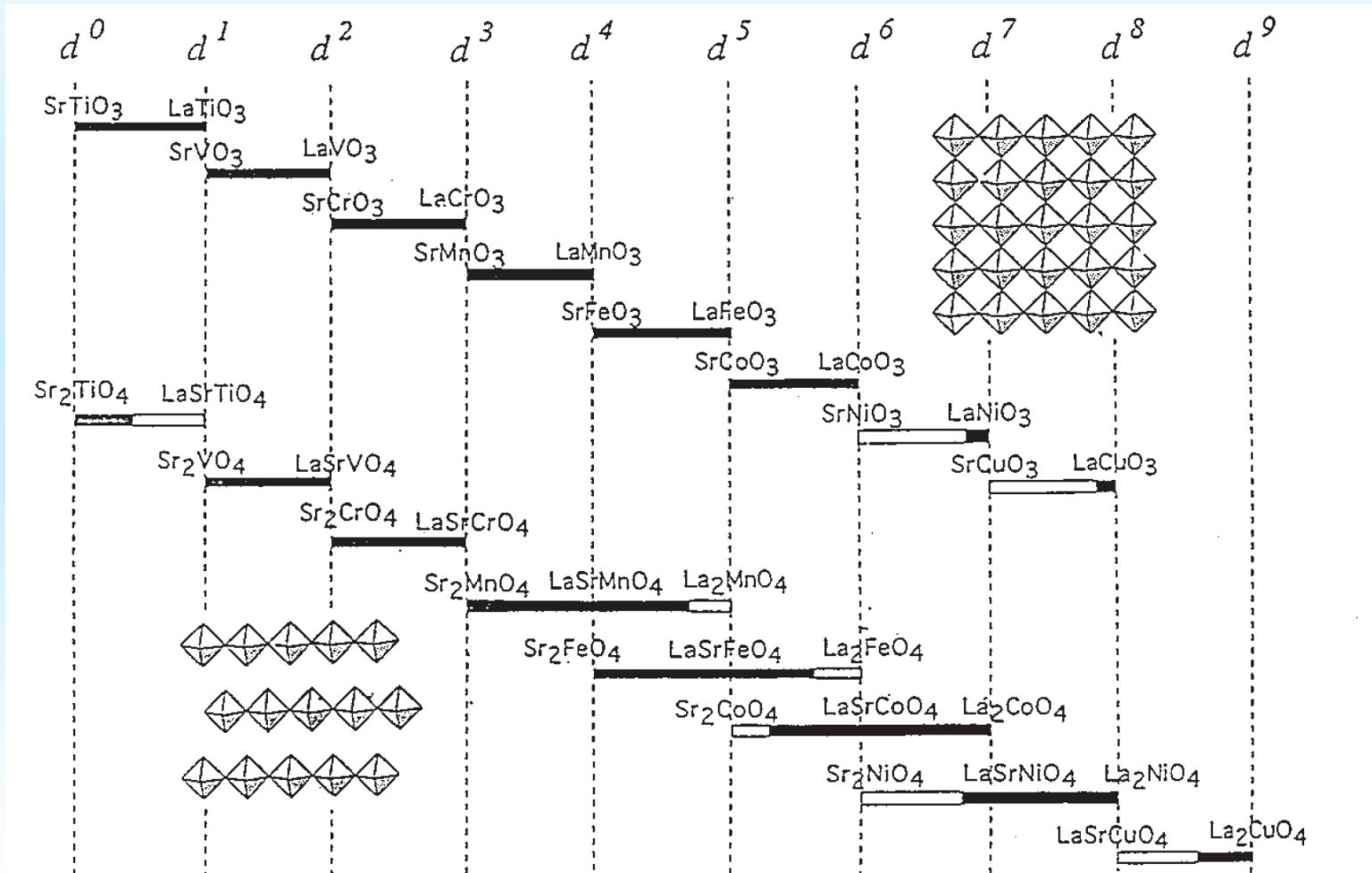
Transition Isolant métal contrôlée par le remplissage dans les pérovkites $La_{1-x}Sr_xVO_3$



Même chose dans les pérovskites au Vanadium



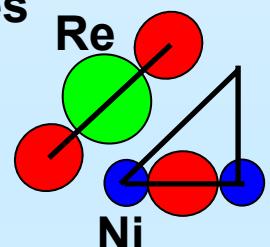
Control du remplissage dans les pérovskites



Transition Isolant métal contrôlée par la largeur de bande dans les pérovskites $ReNiO_3$ (Re = terres rares)

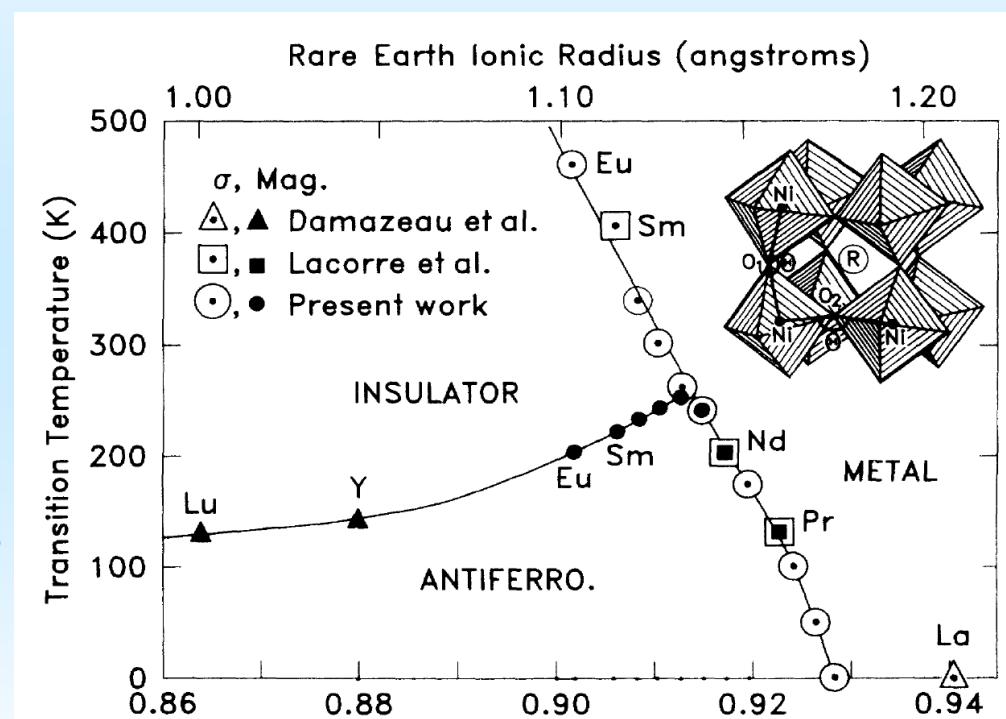
Facteur de tolérance des pérovskites ABO_3 :

$$f = (r_A + r_O) / \sqrt{2(r_B + r_O)}$$



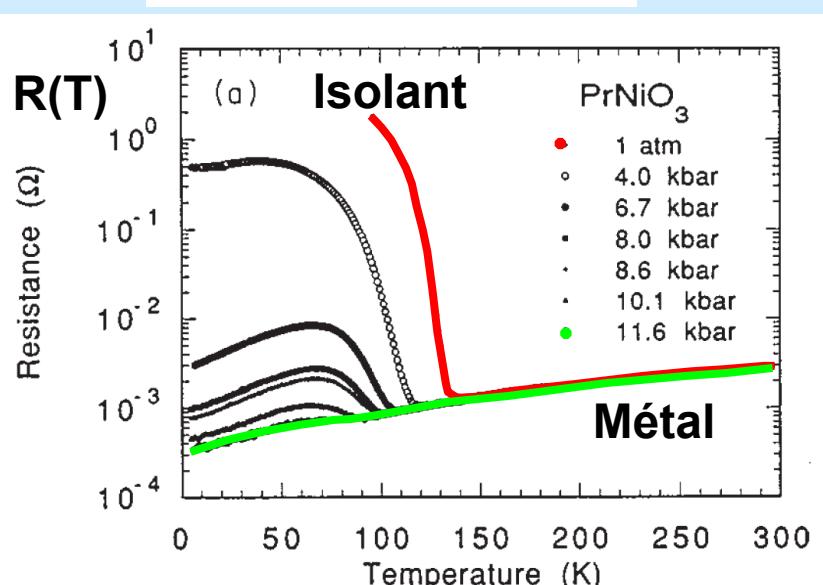
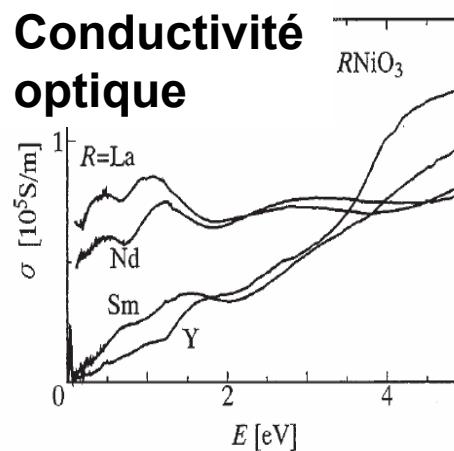
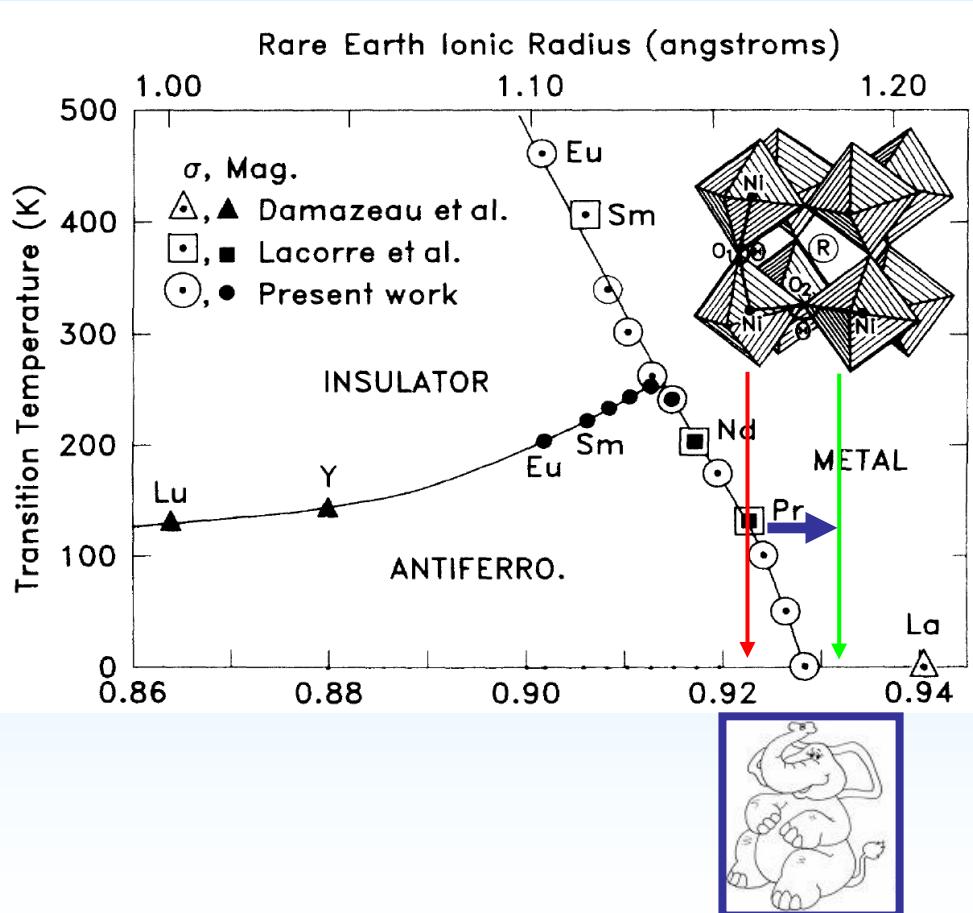
Si $f \approx 1$ pérovskite cubique

Si $f < 1$ (r_A trop petit) transition vers pérovskite orthorhombique $GdFeO_3$

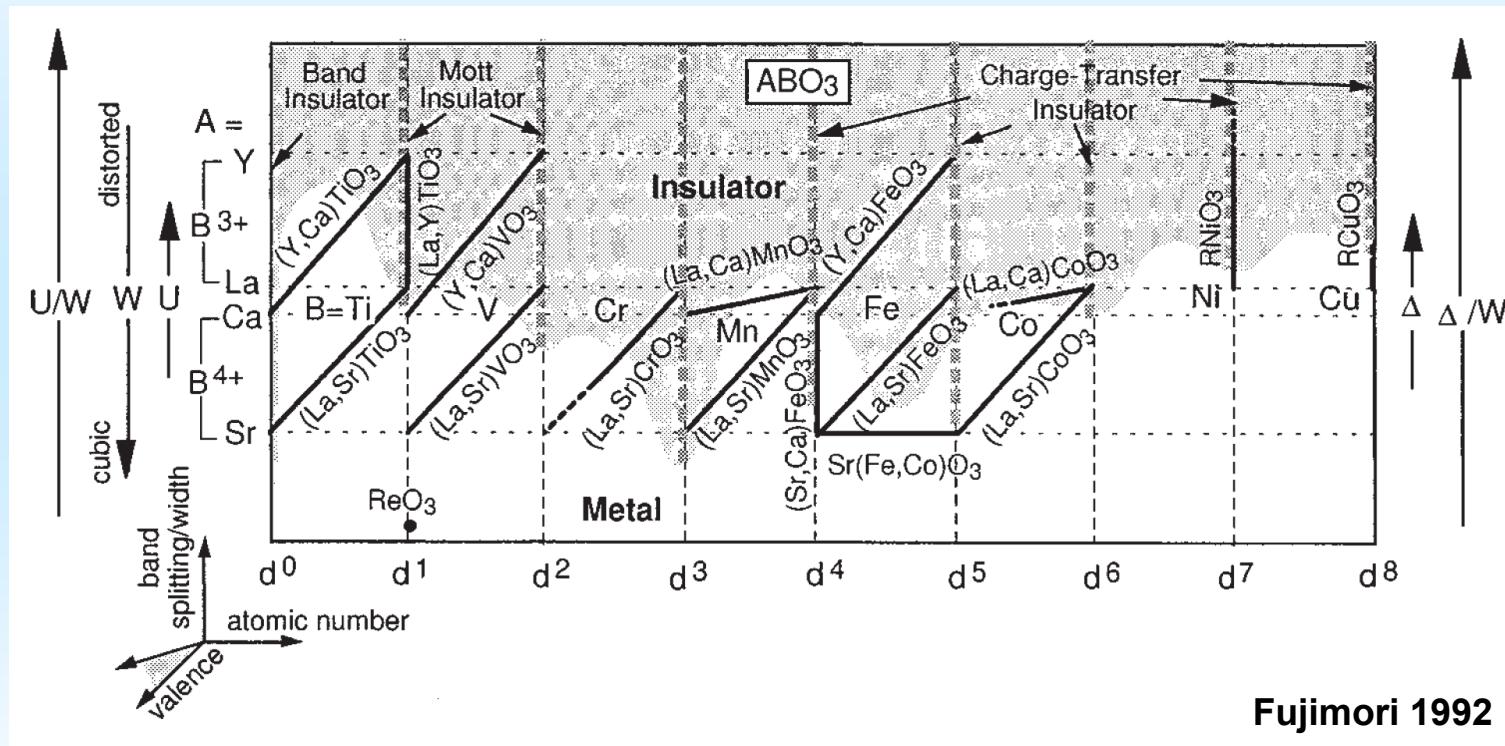


La distorsion permet de jouer sur la largeur de bande → TMI

Transition Isolant métal contrôlée par la largeur de bande dans les pérovskites $ReNiO_3$ (Re = terres rares)

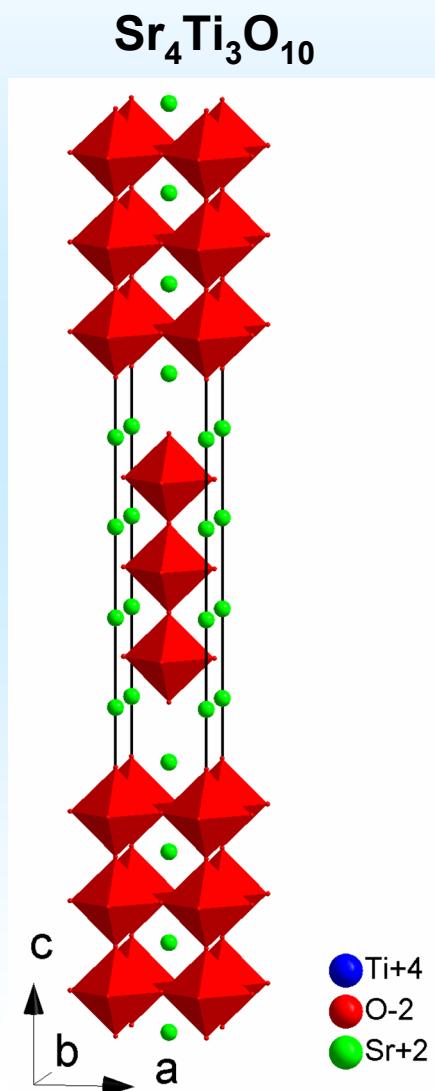
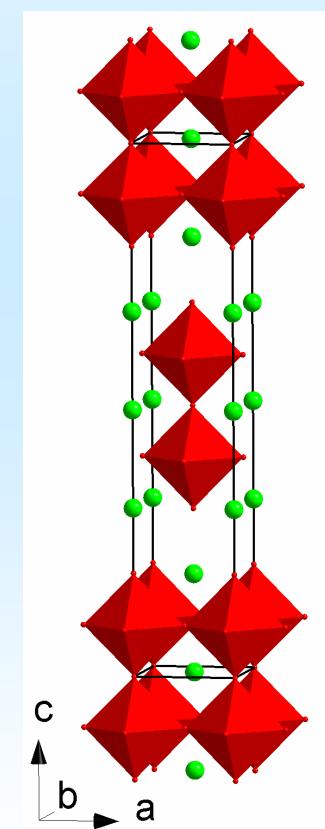
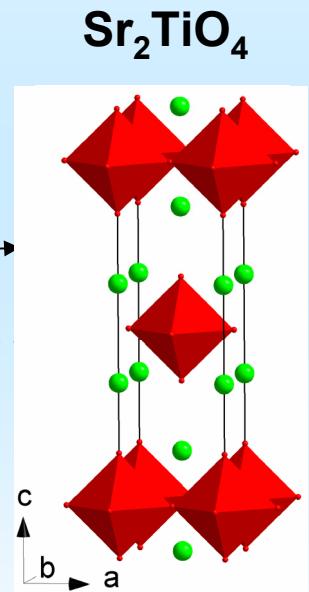
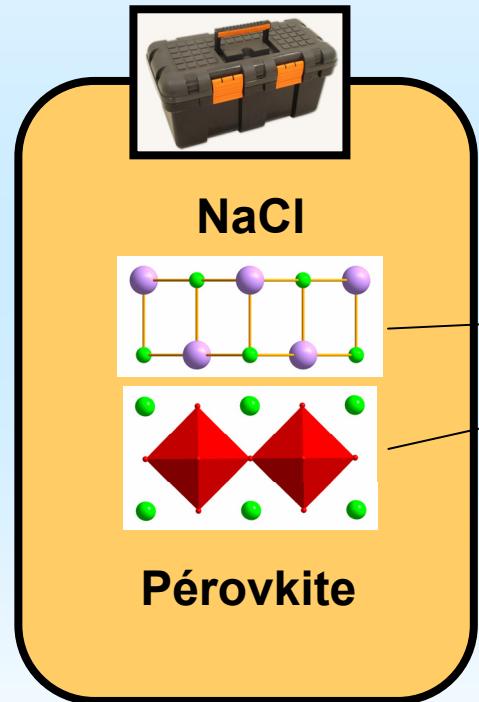


Transition Isolant métal contrôlée par la largeur de bande dans les pérovskites $ReNiO_3$ (Re = terres rares)



Rationalisation TMI dans pérovskites

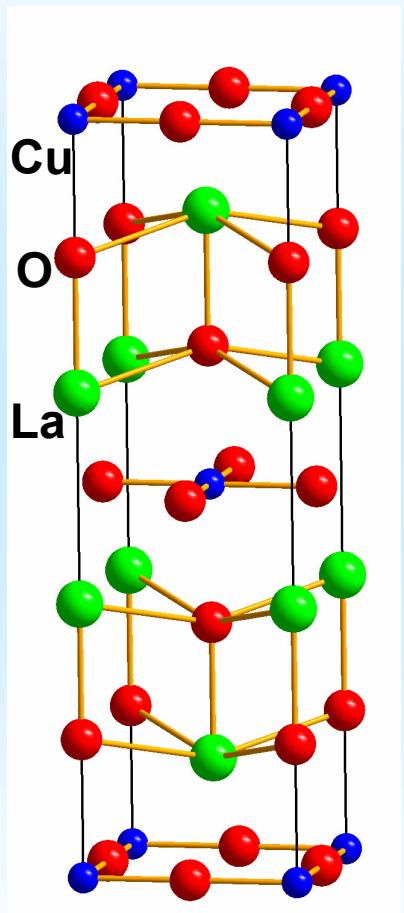
La série d'homologue Ruddlesden-Popper



Intercroissance de feuillets types NaCl et Pérovskite

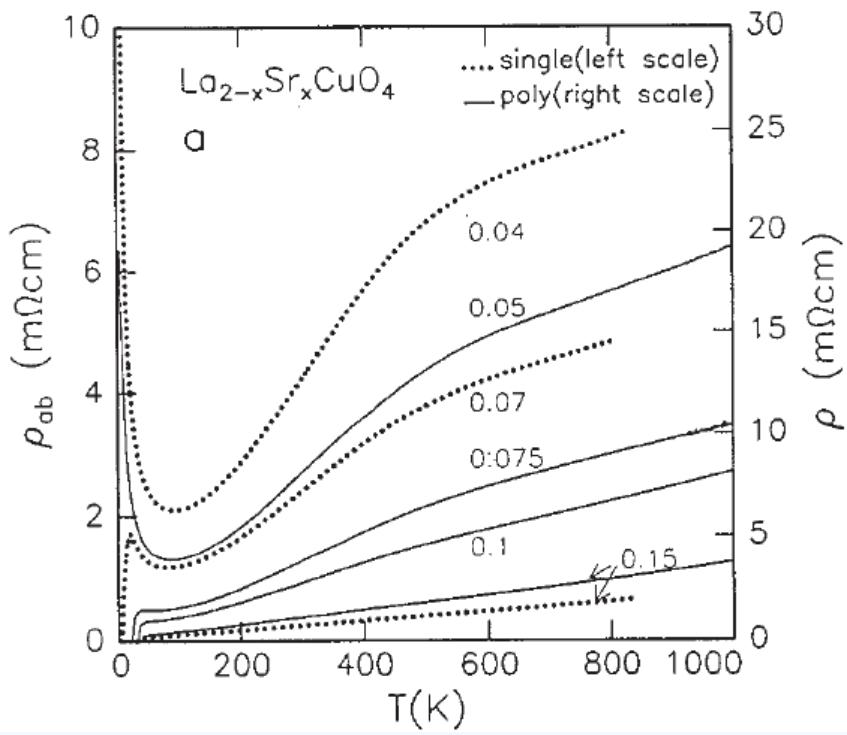
Formulation générale $\text{A}_{n+1}\text{M}_n\text{O}_{3n+1}$

Les cuprates supraconducteurs



$\text{La}_2\text{Cu}^{2+}\text{O}_4$
Phase RP n=1
Isolant de Mott

TMI par dopage trou

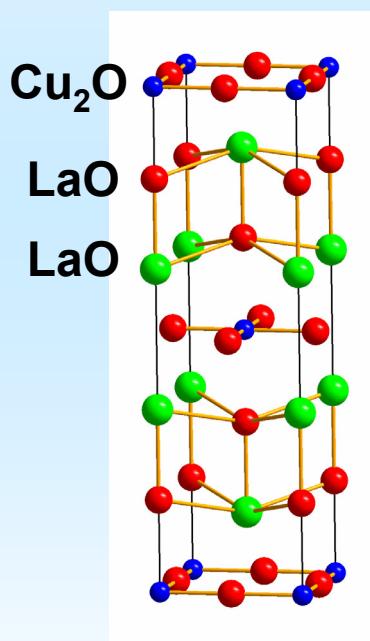


Supra ! $T_c \approx 40\text{K}$

1986 Bednorz et Müller supraconductivité dans le composé $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$
Z. Physik B, 64, 189 (1986)

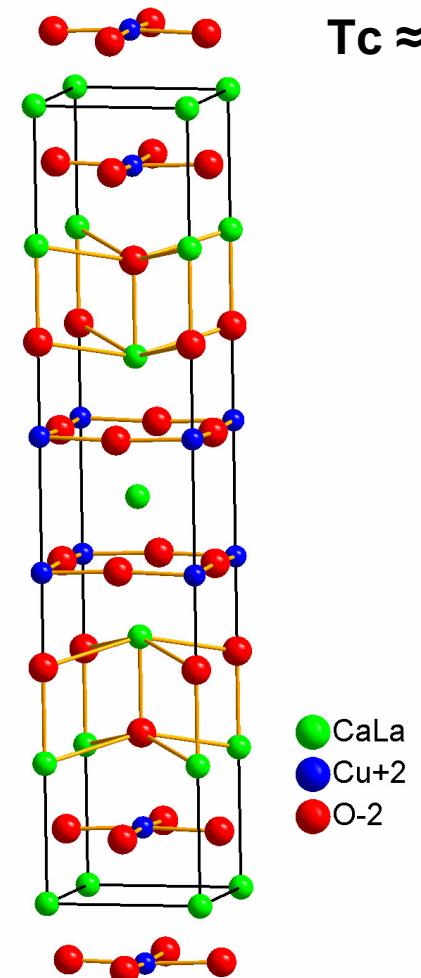
Les HTc cuprates supraconducteurs

La_2CuO_4
Phase RP n=1



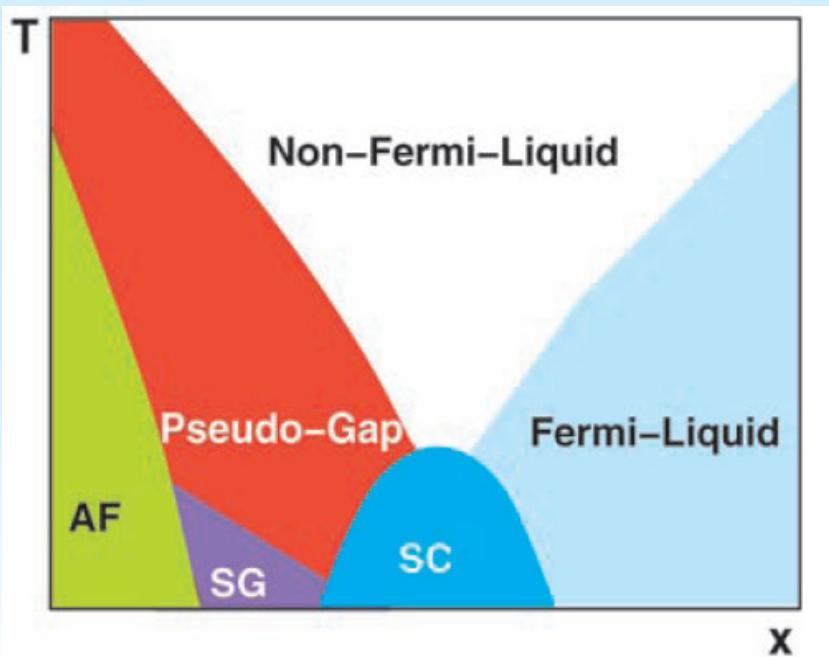
$T_c \approx 40\text{K}$

$\text{La}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_6$ Phase RP n=2



$T_c \approx 60\text{K}$

Diagramme de phase générique

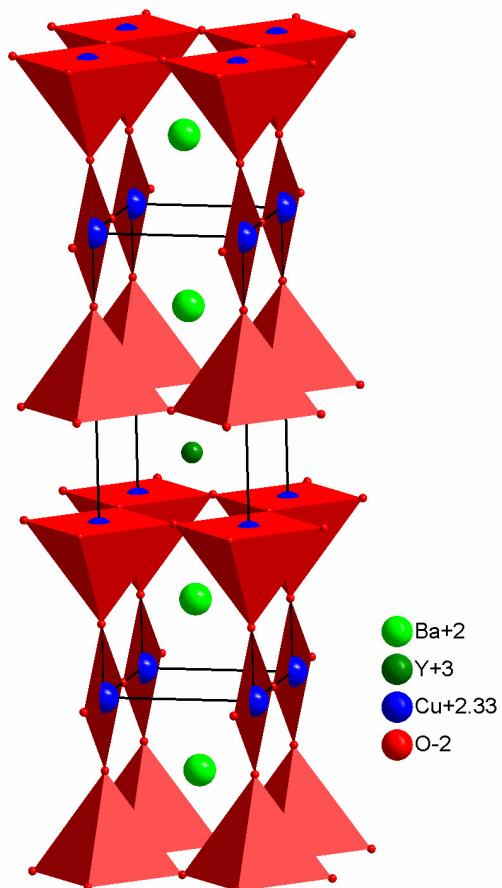


Plan CuO_2 dopé ≈ 0.2 trou
= HTc supraconductivité

Relation « structure propriétés »

Les HTc cuprates supraconducteurs

$\text{Ba}_2\text{YCu}_3\text{O}_7$ Pérovskite déficiente en O



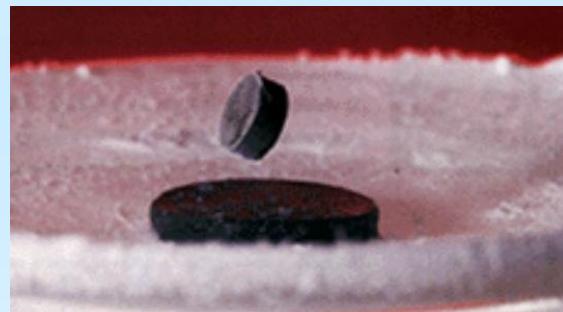
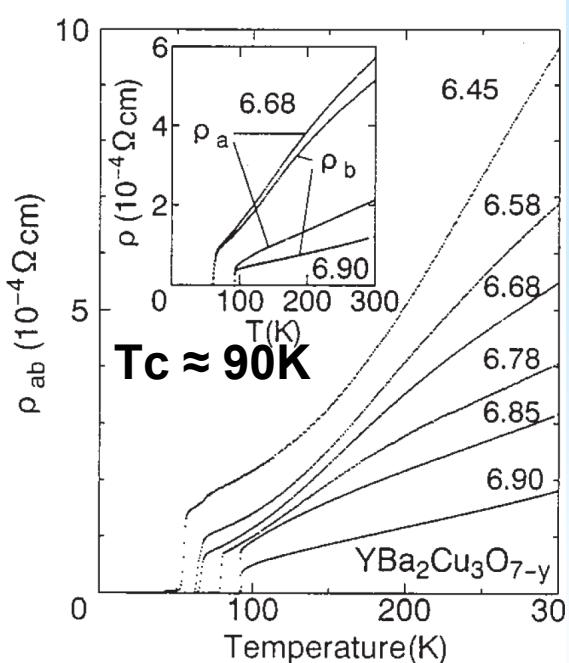
VOLUME 58, NUMBER 16

PHYSICAL REVIEW LETTERS

20 APRIL 1987

Bulk Superconductivity at 91 K in Single-Phase Oxygen-Deficient Perovskite $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$

R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika,
E. A. Rietman, S. Zahurak, and G. P. Espinosa
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 5 March 1987)



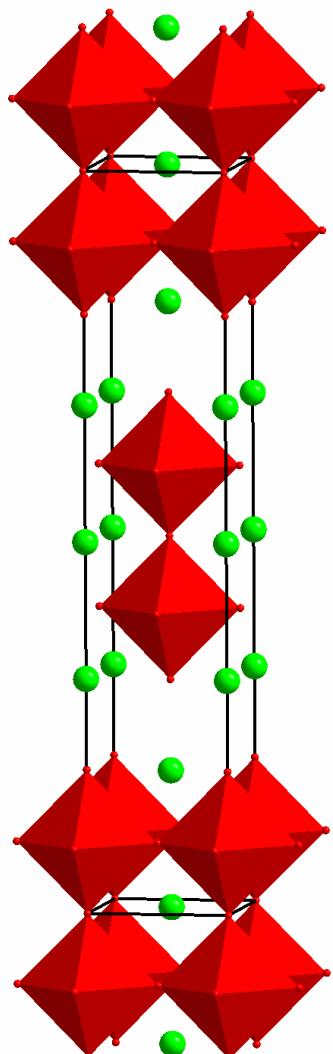
Et puis
 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ $T_c = 85 \text{ K} \dots$

Nature 363, 56 - 58 (06 May 1993)

Superconductivity above 130 K in
Hg–Ba–Ca–Cu–O

A. Schilling, M. Cantoni, J. D. Guo & H. R. Ott

Autres phases Ruddlesden Popper : les manganites

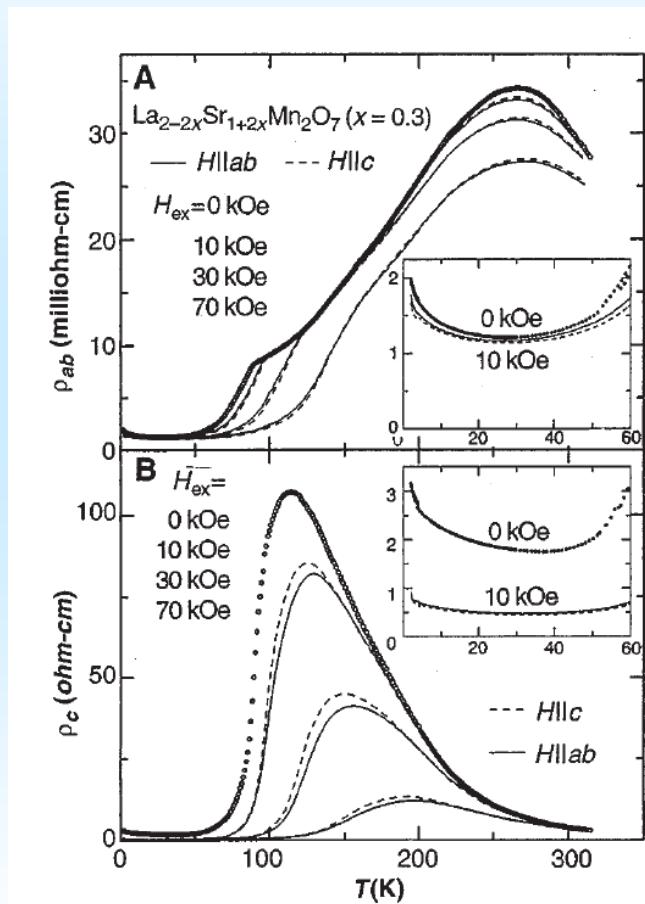
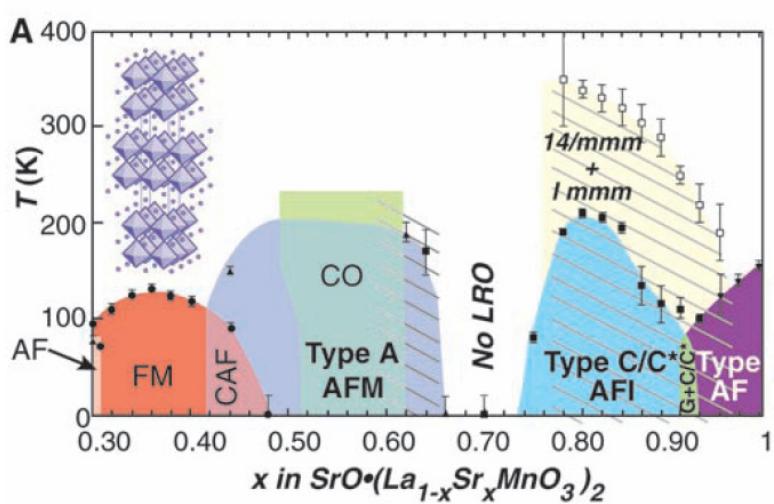


Phase RP n=2



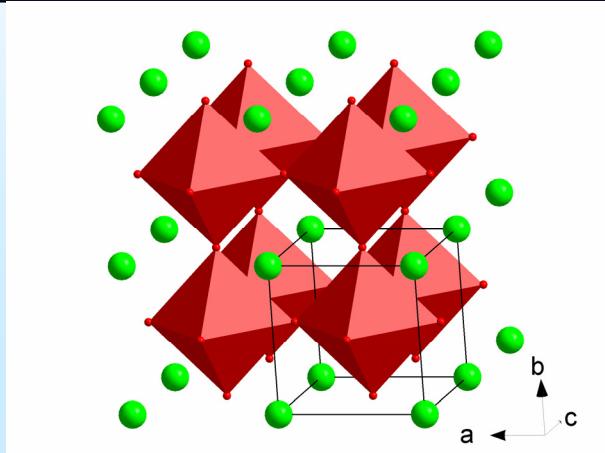
Isolant de Mott pour $x=0$

Dopage $\rightarrow \text{Mn}^{4+}$
Transition Isolant Métal
Magnétorésistance colossale

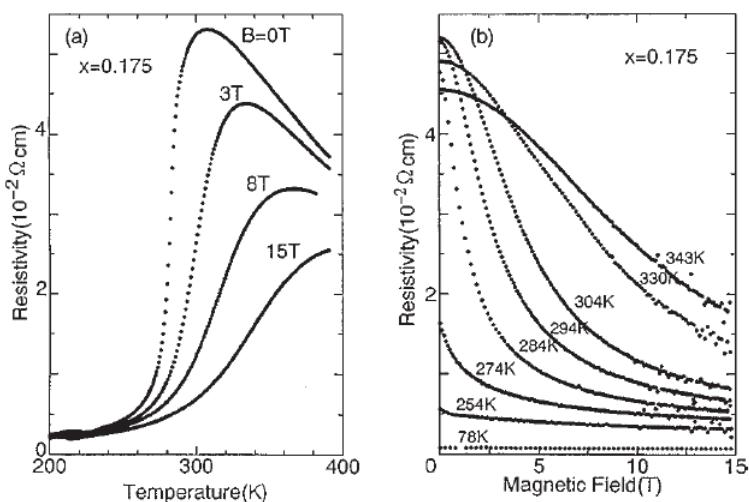


Couplage entre degrés de liberté de charge de spin et orbitaux

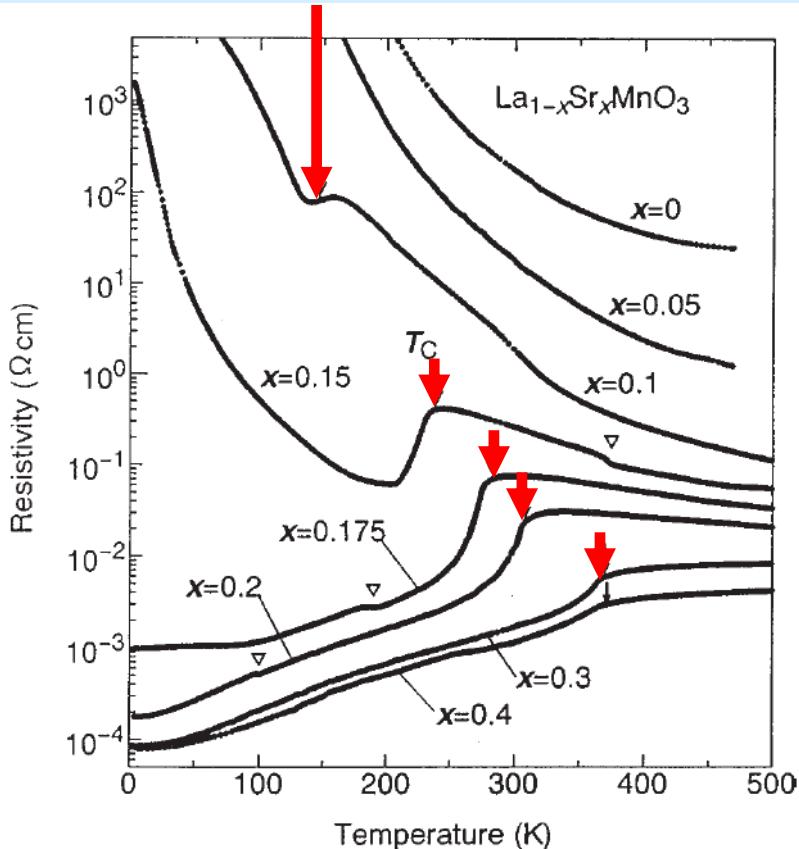
Magnétorésistance négative Colossale : Pérovskite $La_{1-x}Sr_xMnO_3$



Magnétorésistance négative

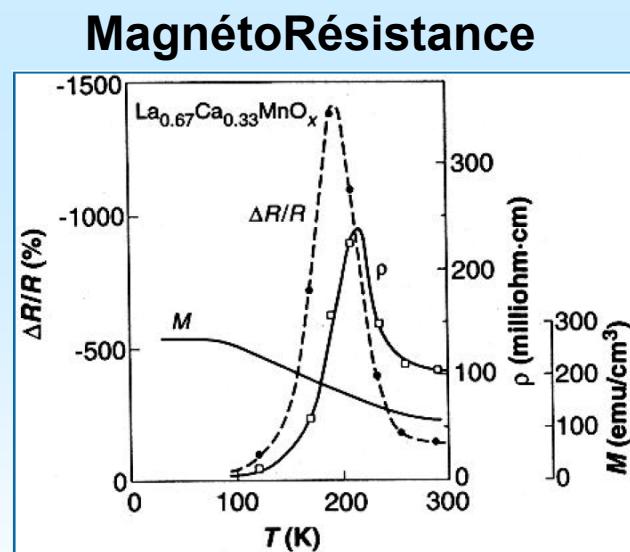
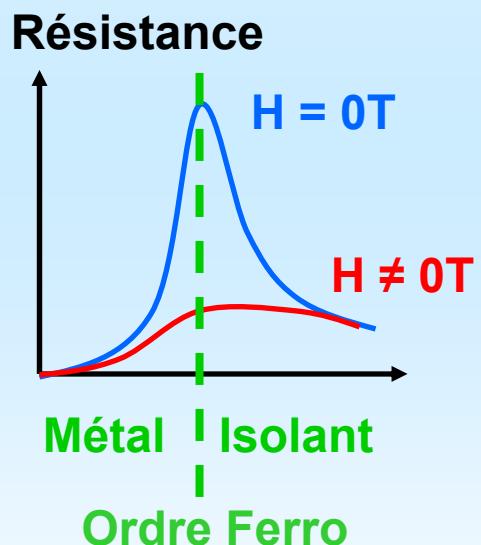
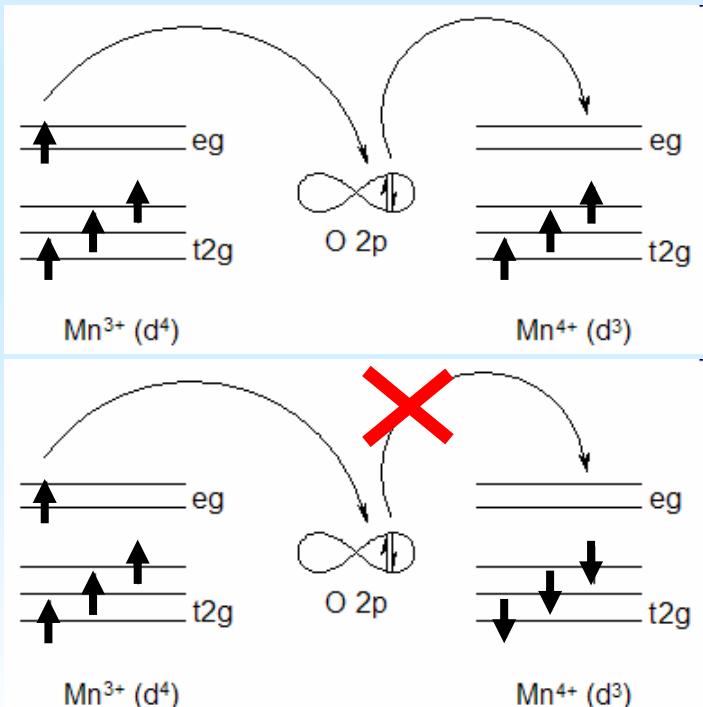


TMI par dopage trou
Ordre
Ferromagnétique



Magnétorésistance négative Colossale : mécanisme de double échange

Règle de Hund les électrons e_g induisent une interaction ferromagnétique

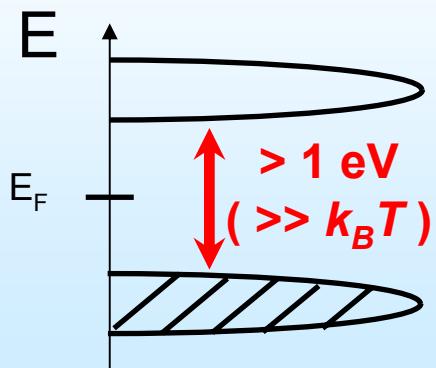


Science 15 April 1994:
Thousandfold Change in Resistivity in
Magnetoresistive La-Ca-Mn-O Films

S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and Chen

Valence mixte $\text{Mn}^{3+}/\text{Mn}^{4+}$

Magnétisme des isolants de Mott

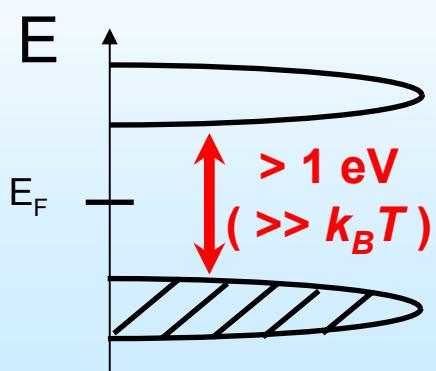


d° liberté
de spin

d° liberté
de charge

d° liberté
orbital

Magnétisme des isolants de Mott

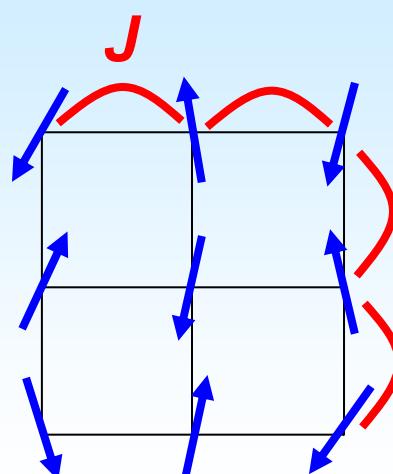
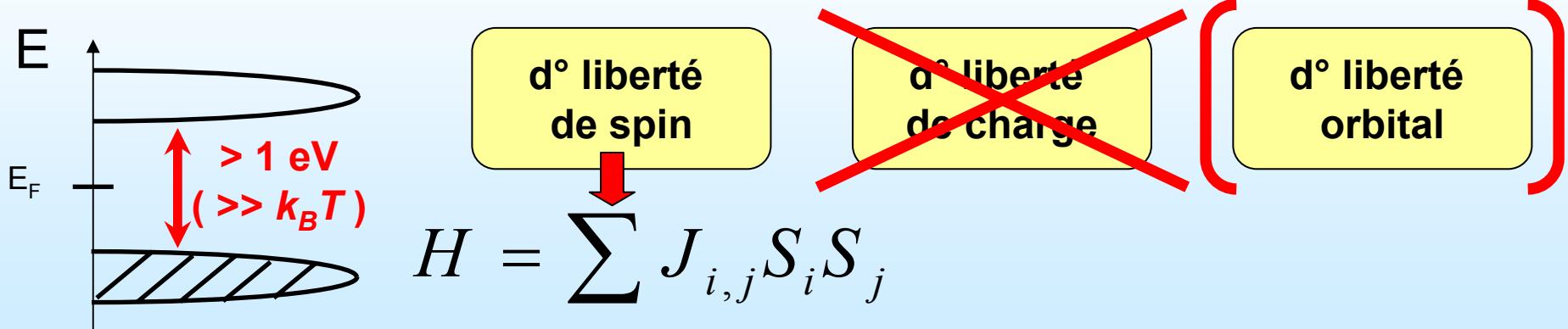


d° liberté de spin

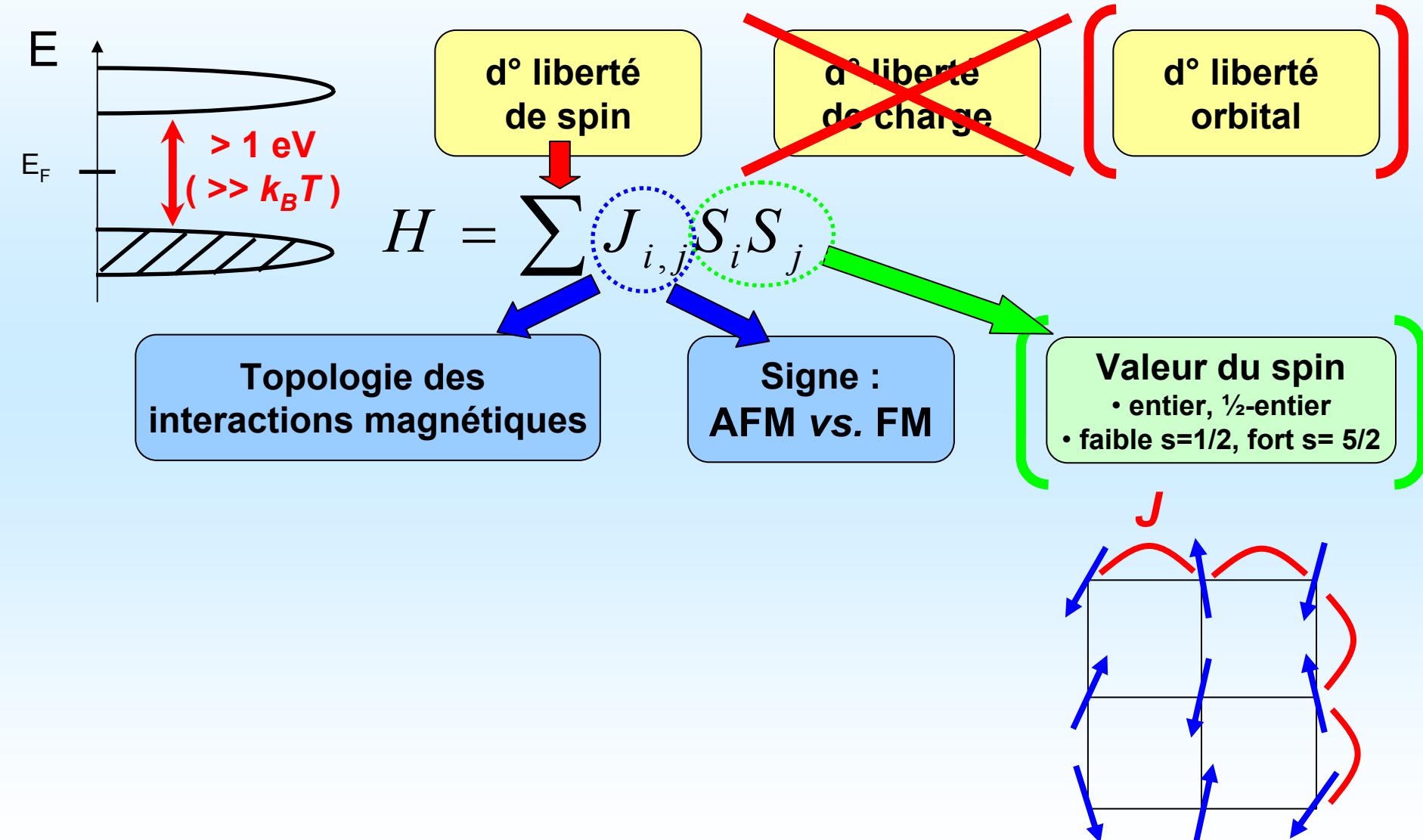
~~d° liberté de charge~~

d° liberté orbital

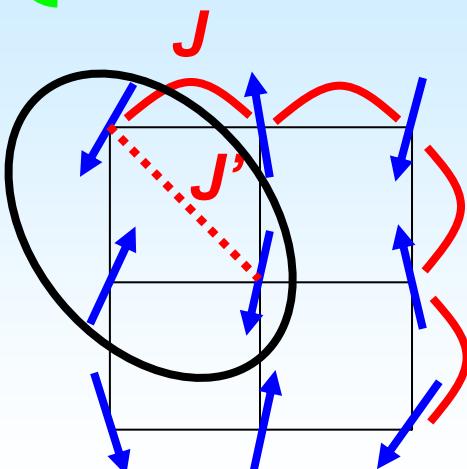
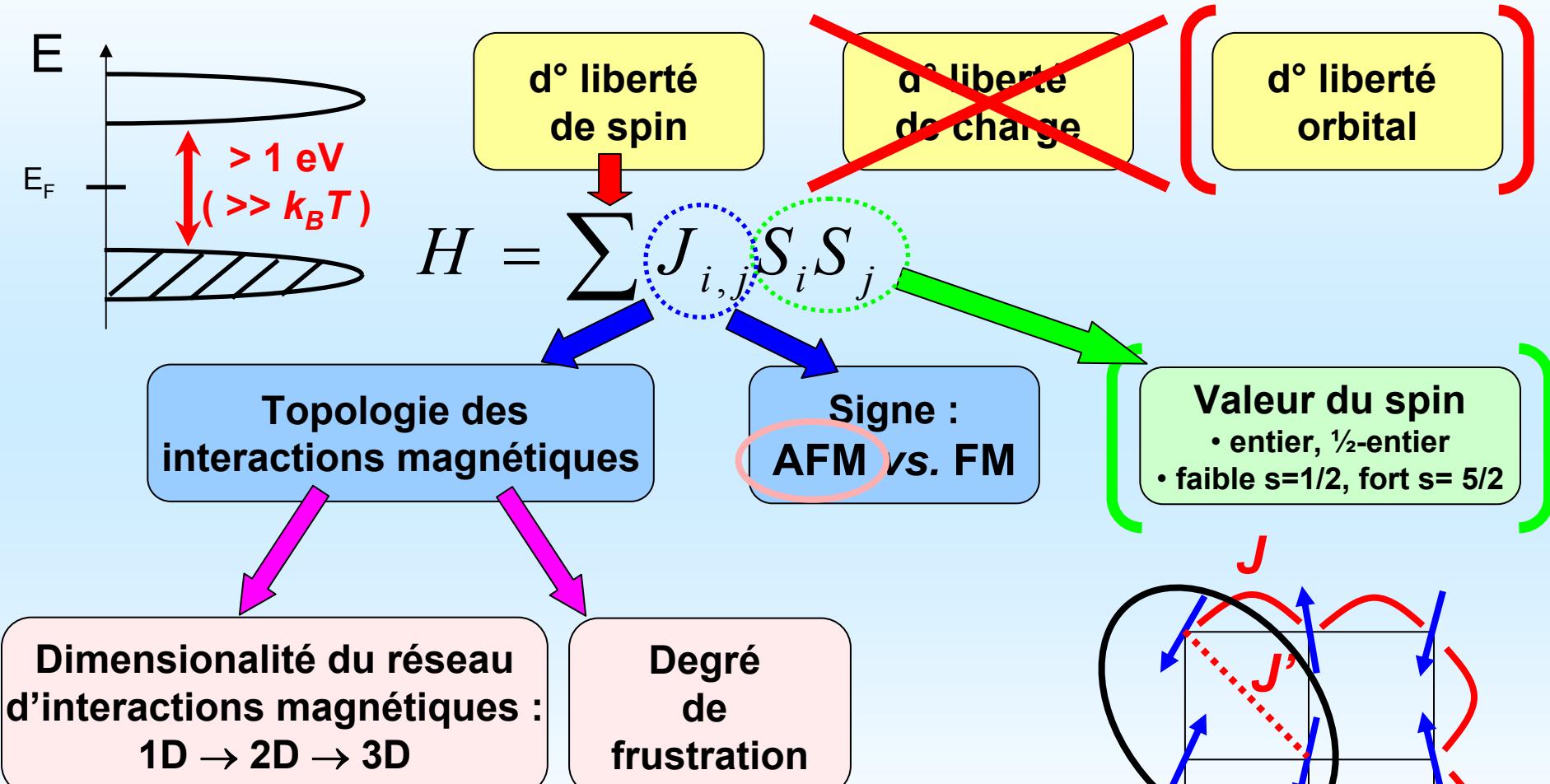
Magnétisme des isolants de Mott



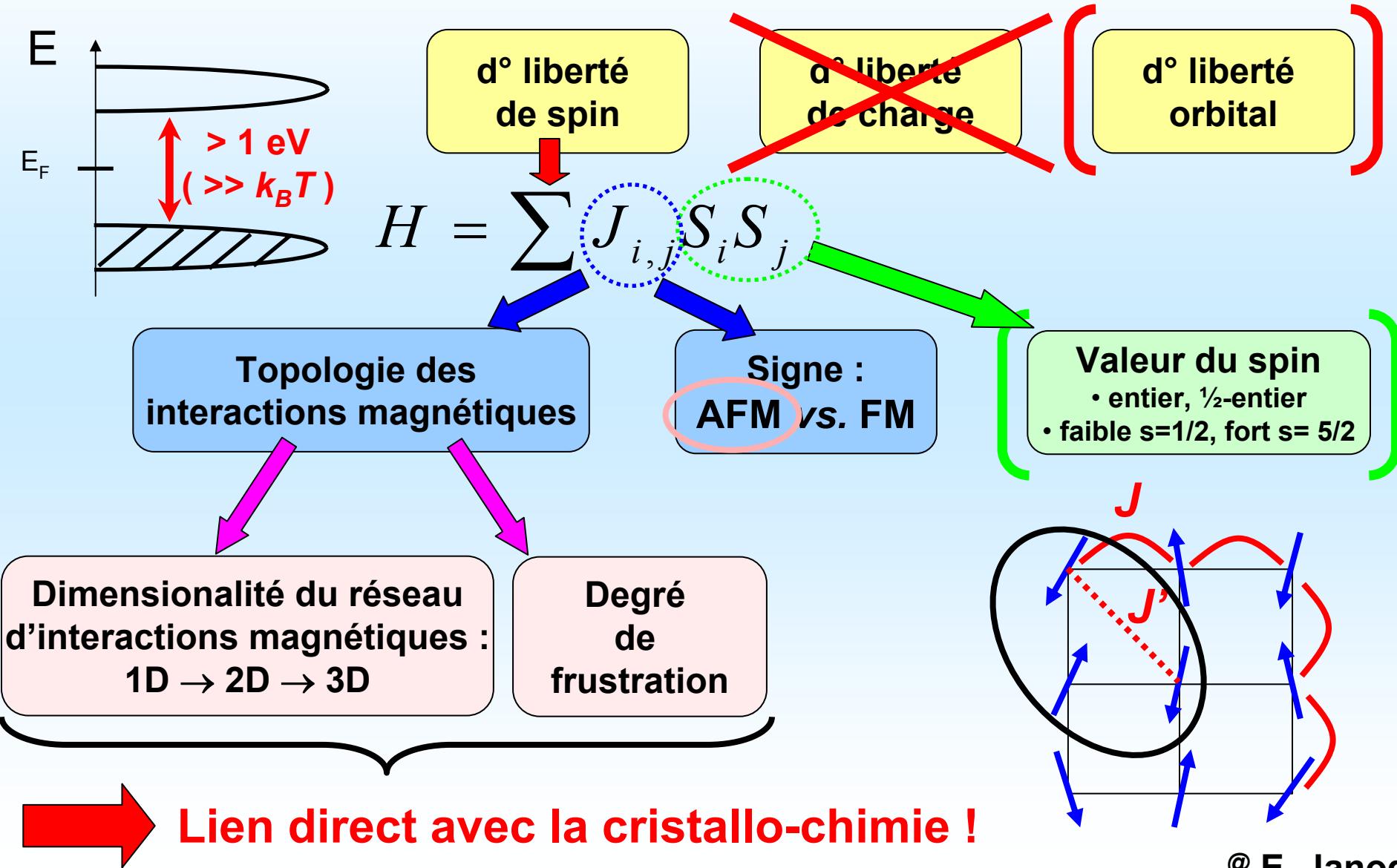
Magnétisme des isolants de Mott



Magnétisme des isolants de Mott



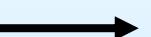
Magnétisme des isolants de Mott



Magnétisme des isolants de Mott

Série homologue $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ (Z. Hiroi et al., JSSC 95, 230 (1991))

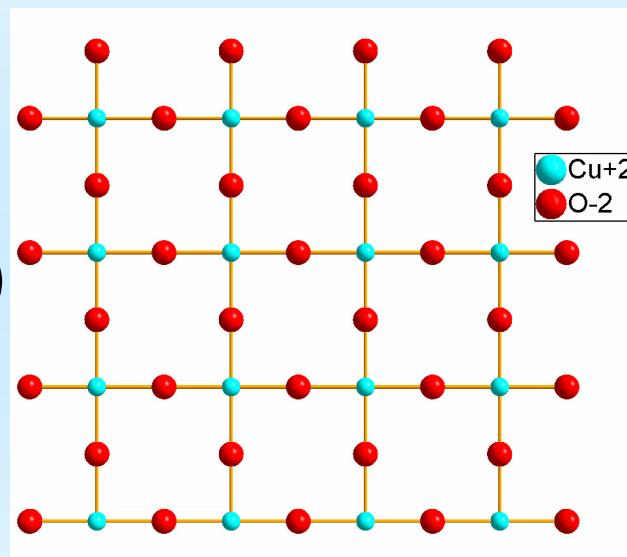
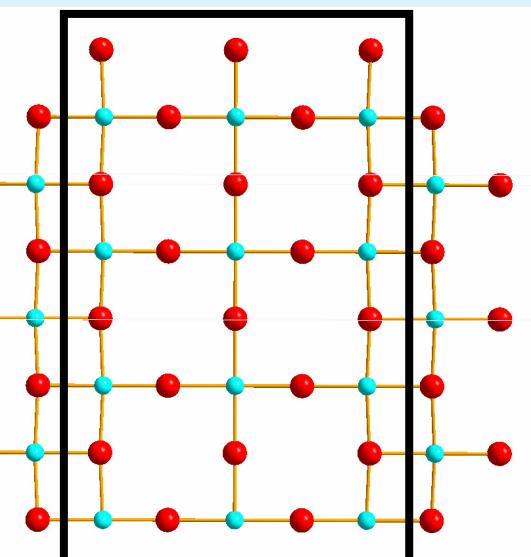
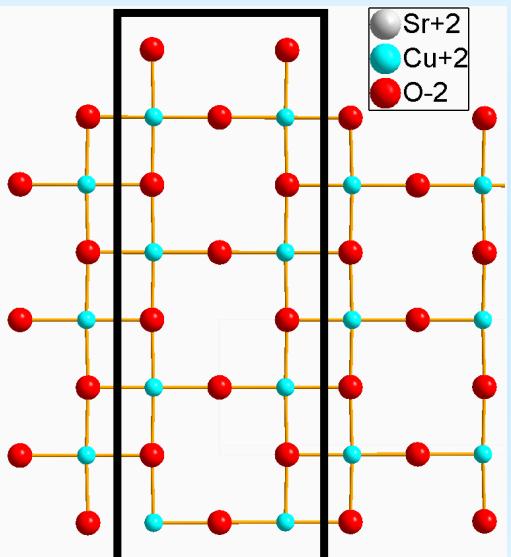
SrCu_2O_3 ($n = 3$)



$\text{Sr}_2\text{Cu}_3\text{O}_5$ ($n = 5$)



$(\text{Ca},\text{Sr})\text{CuO}_2$ ($n = \infty$)



1D

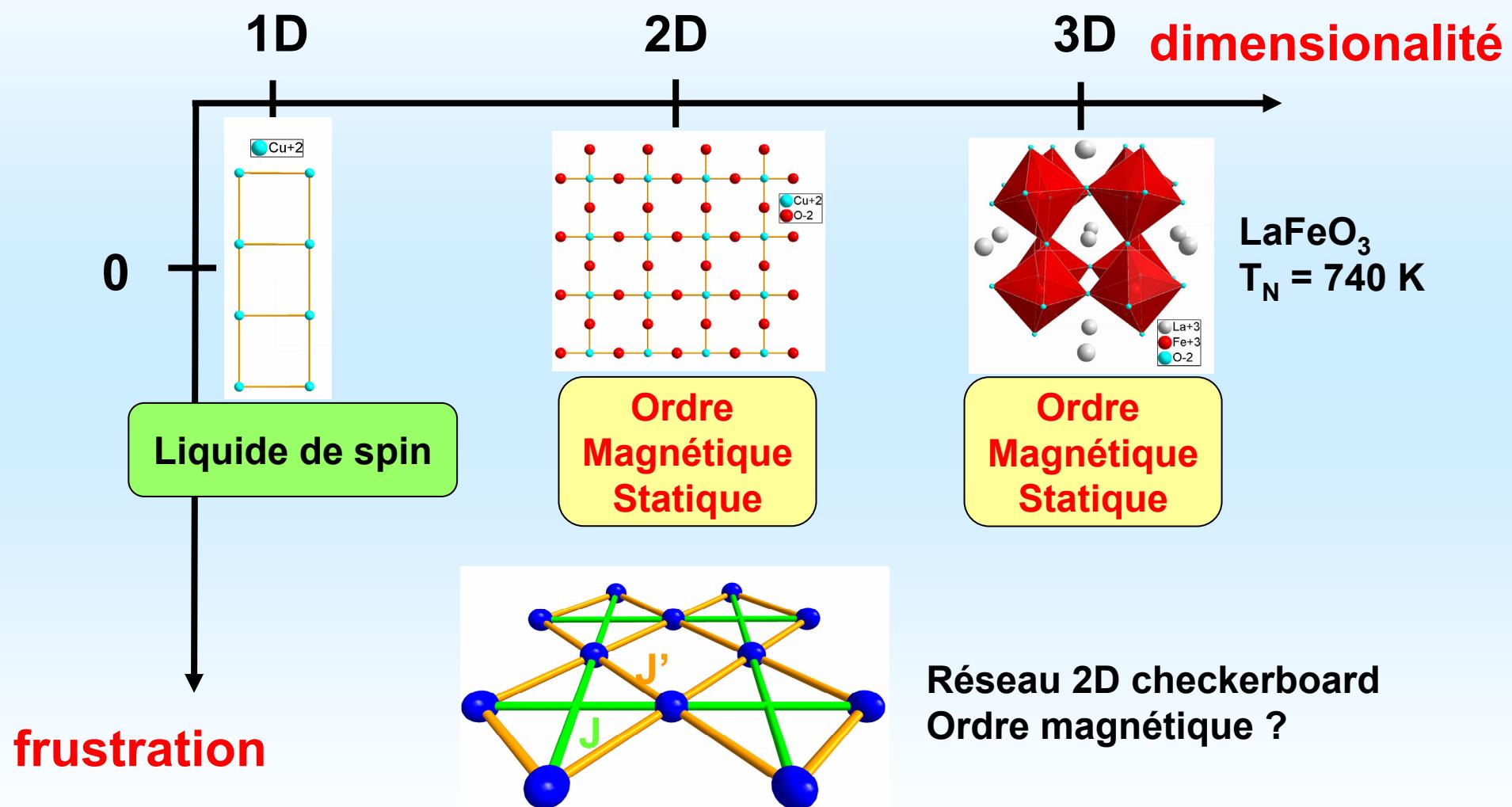


2D

Etat désordonné liquide de spin à $T = 0$ K

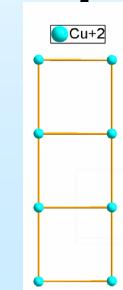
Ordre Magnétique Statique (Néel),
 $T_N = 539$ K

Magnétisme des isolants de Mott



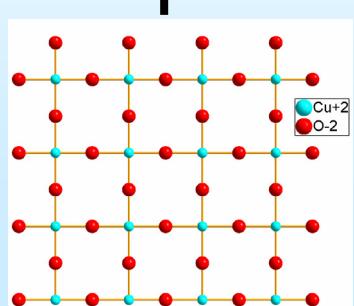
Magnétisme des isolants de Mott

1D



Liquide de spin

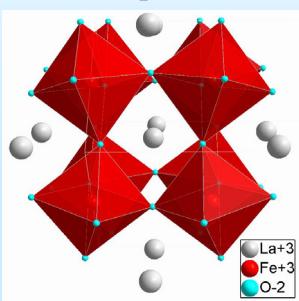
2D



Ordre Magnétique Statique

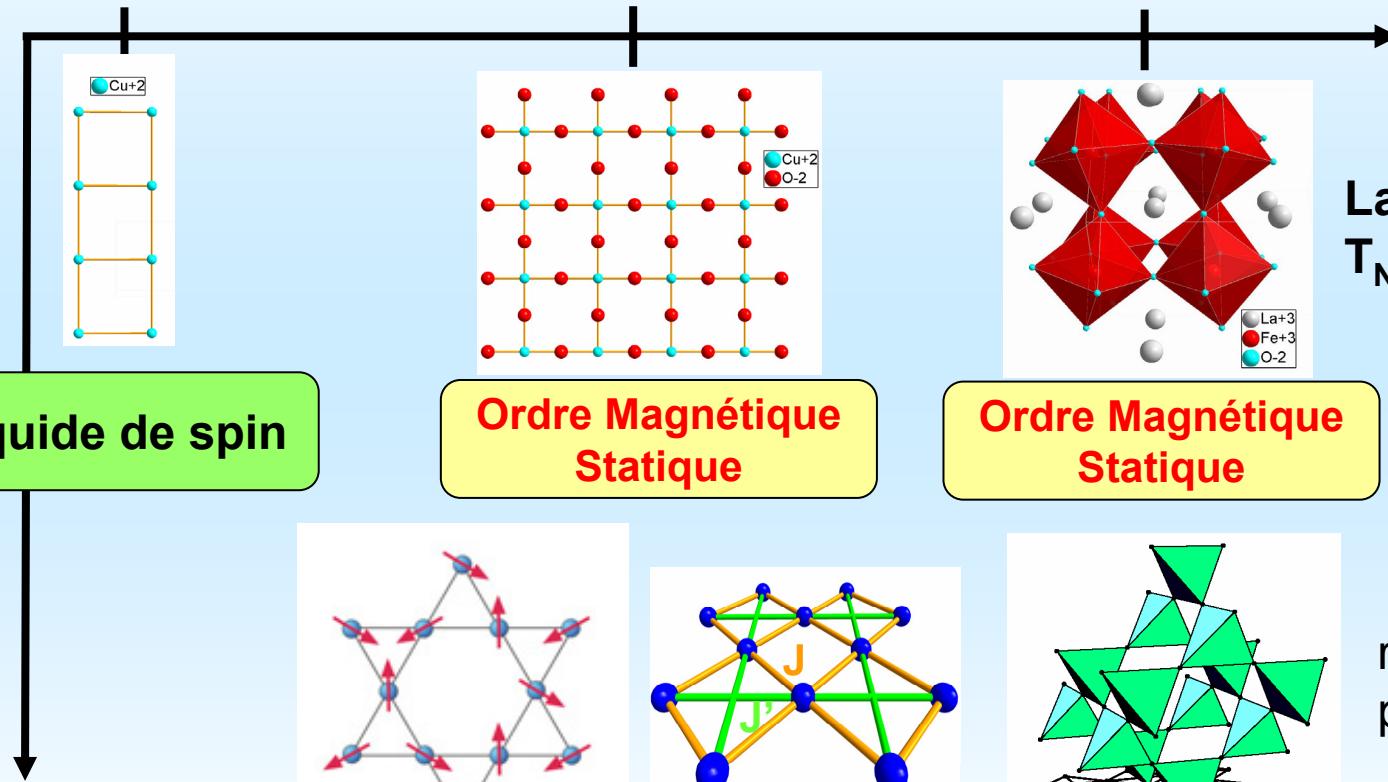
3D

dimensionalité



LaFeO_3
 $T_N = 740 \text{ K}$

Ordre Magnétique Statique



frustration

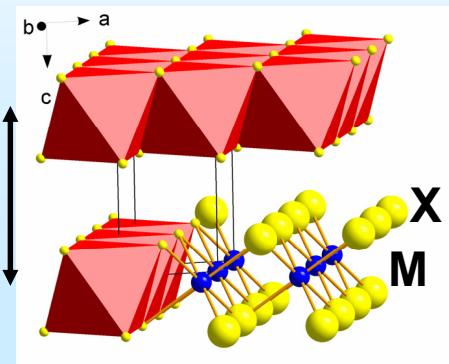
réseau Kagomé Checkerboard

réseau
pyrochlore

2D et 3D frustrés : possibilité d'états fondamentaux
non-magnétiques, non-conventionnels

Dichalcogénures d'éléments de transition MX_2

Structures lamellaires

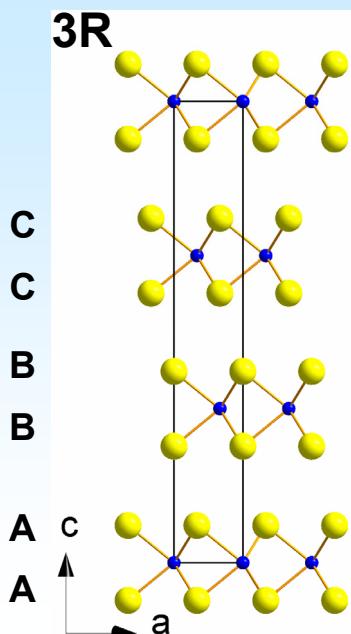
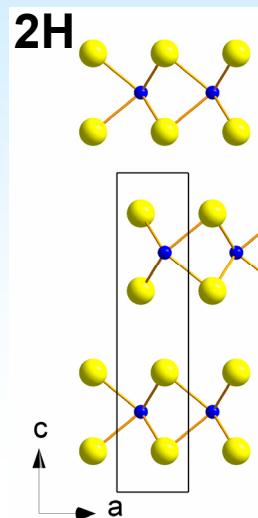


CdI₂



titanium 22 Ti 47.887	vanadium 23 V 50.942	chromium 24 Cr 51.996
zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94
hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84

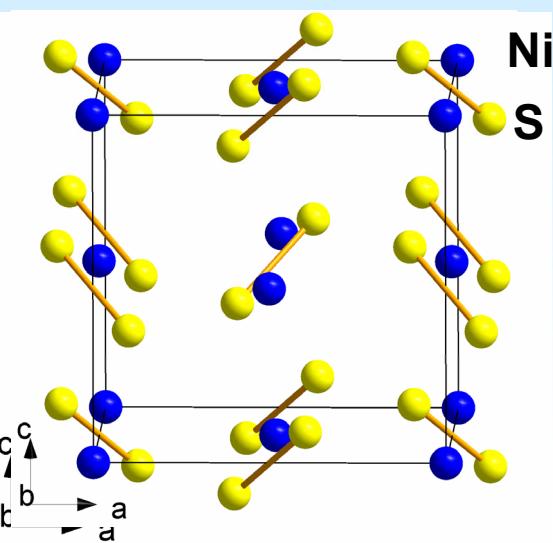
ou MoS₂



Structures 3D



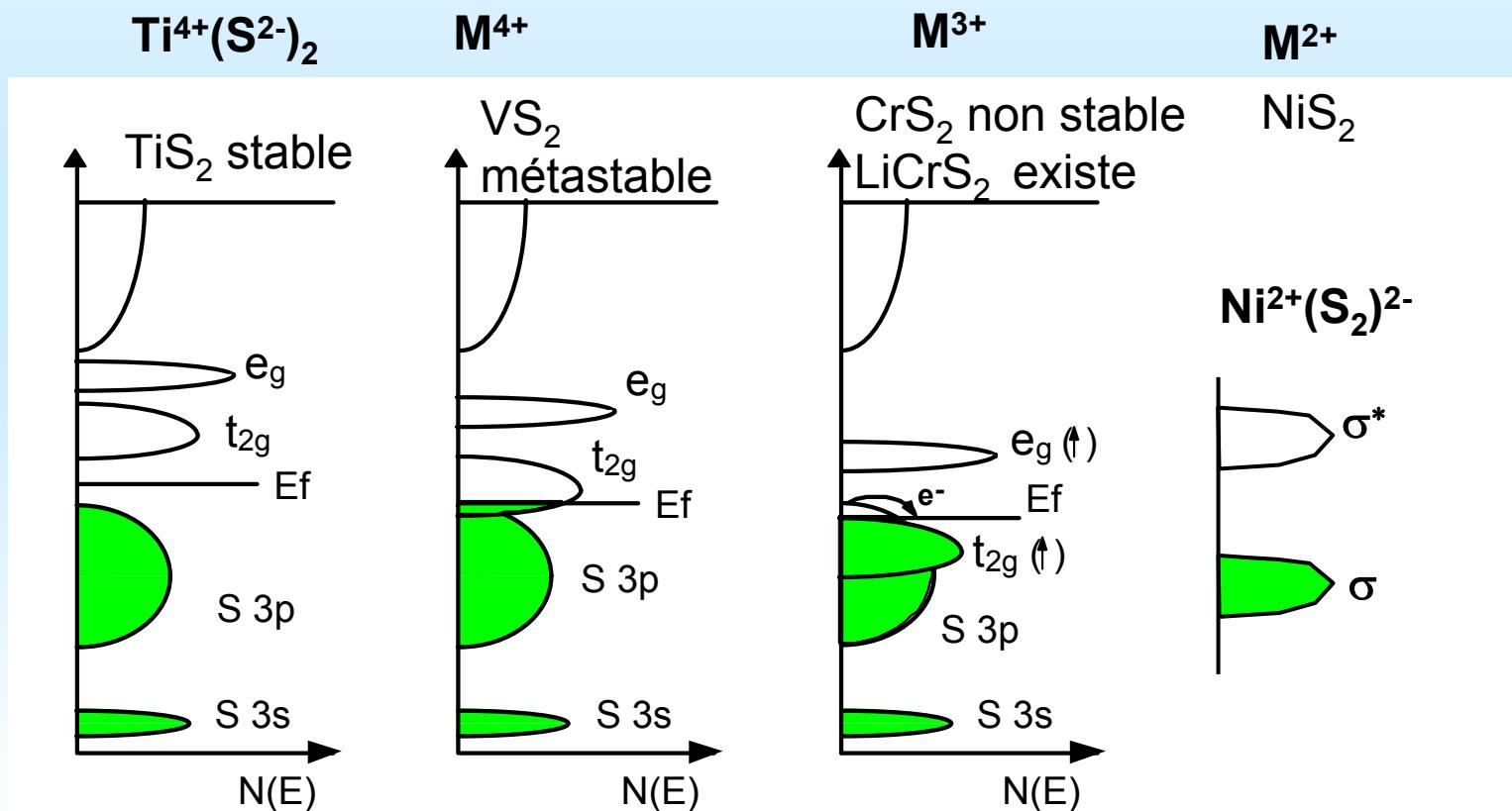
Pyrite ou marcassite



TX_2 un cas de compétition redox à l'état solide

titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546
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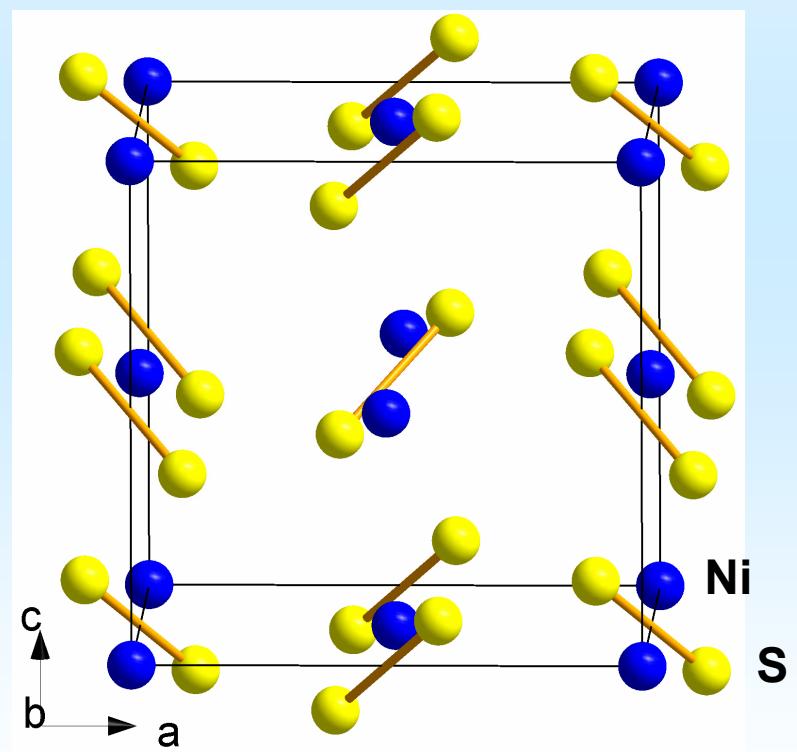
Abaissement des niveaux d



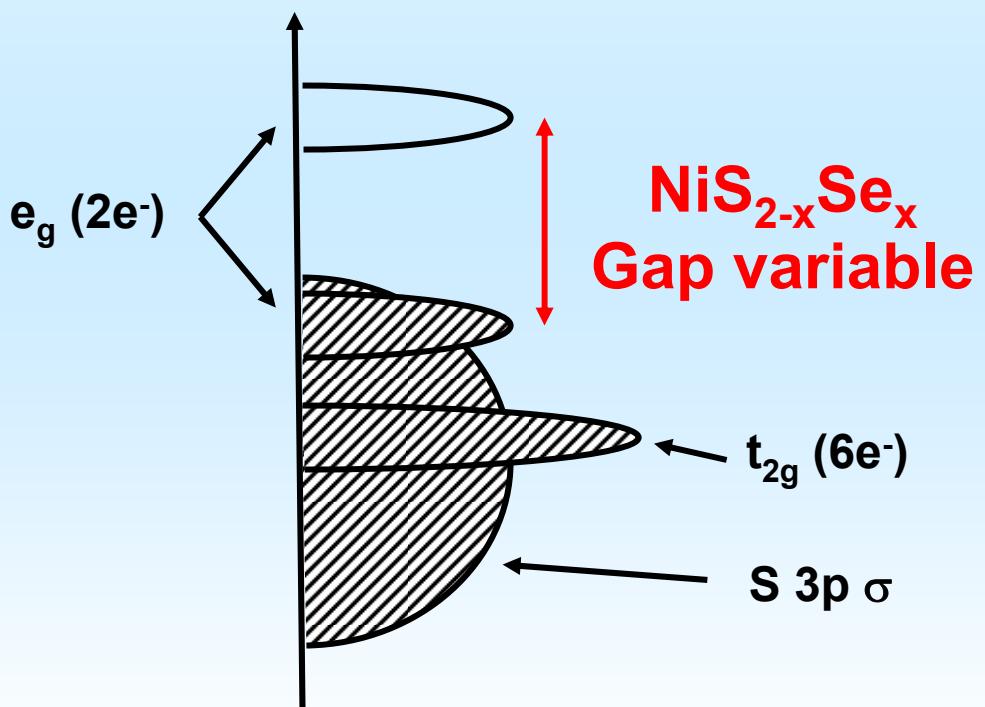
M^{4+} instable $\rightarrow \text{M}^{+2}$ oxydation du soufre et formation de paires $(\text{S}_2)^{2-}$

La transition de Mott dans $NiS_{2-x}Se_x$

Structure pyrite (cubique)



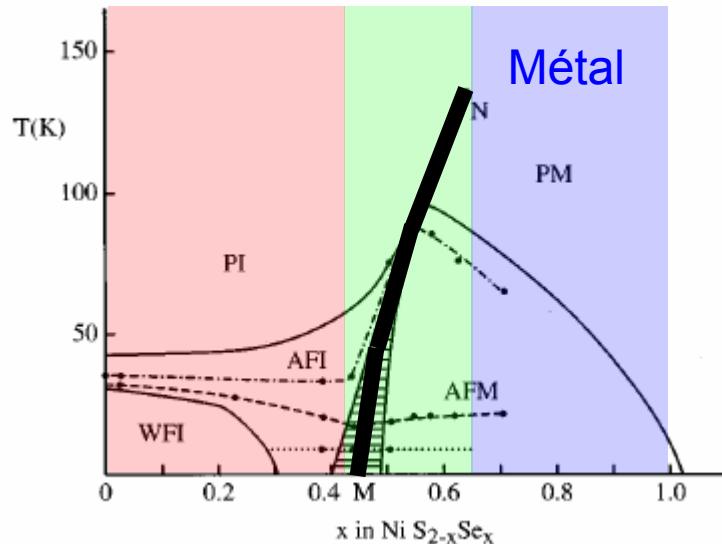
NiS_2 Isolant Mott – gap $\sim 0.5\text{eV}$



$NiSe_2$ métal

La transition de Mott dans $NiS_{2-x}Se_x$

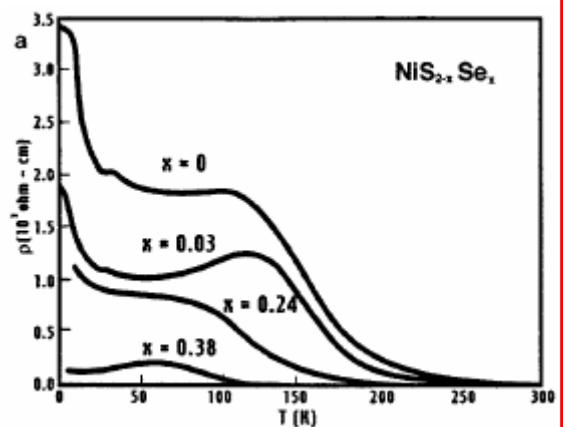
Diagramme phase et résistivité :



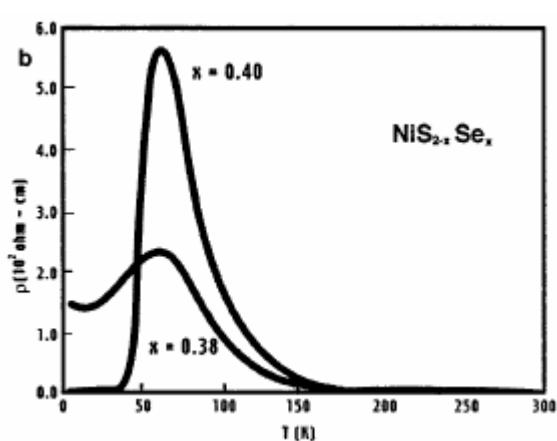
Pression chimique ou physique



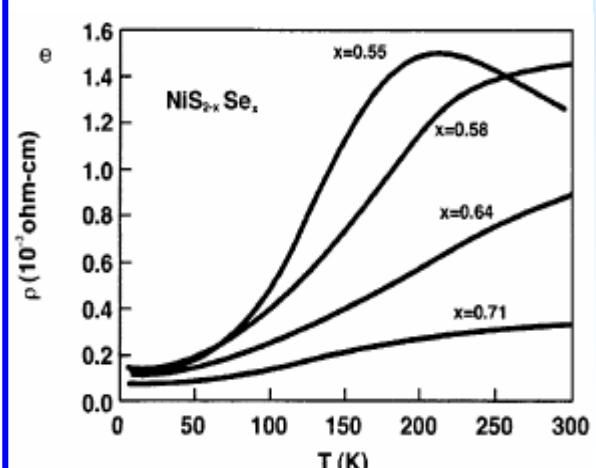
Isolant



Transition de Mott

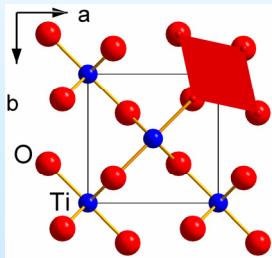


Métal

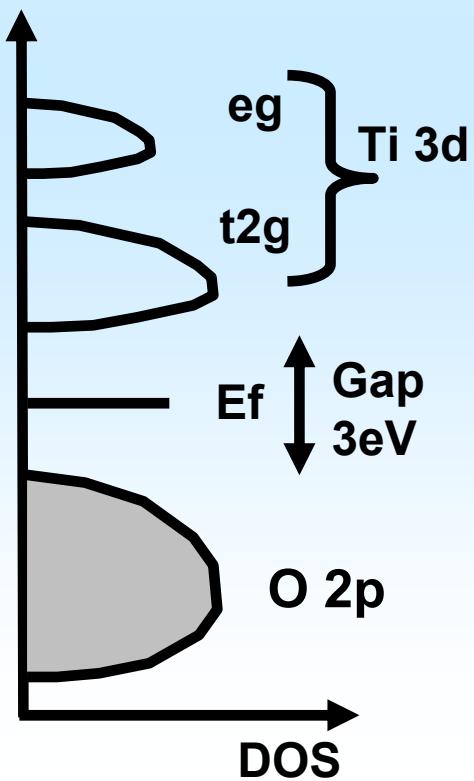


Série TiX_2 ($X=S, Se, Te$) : transition isolant semi-métal

TiO_2
Rutile

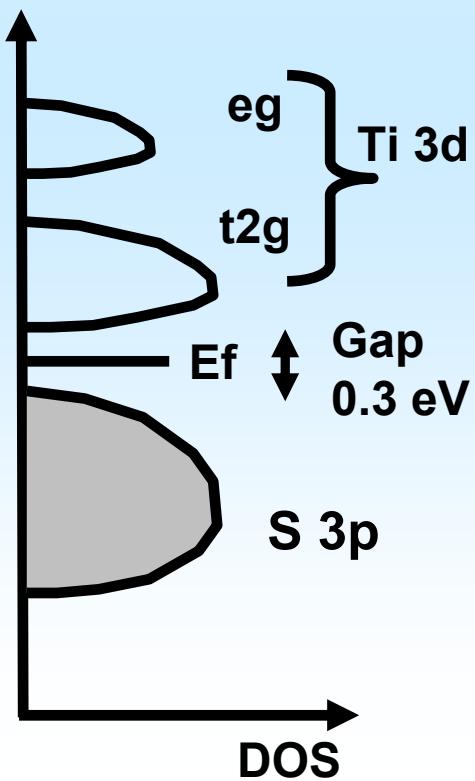


Energie



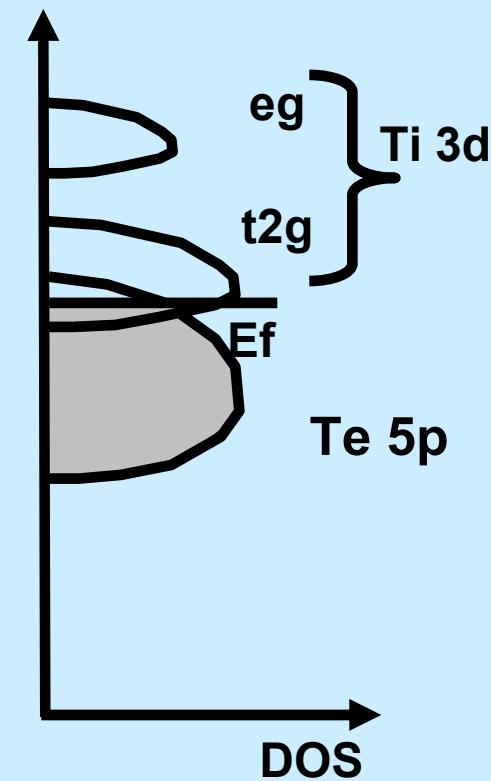
TiS_2 semi-conducteur

Energie



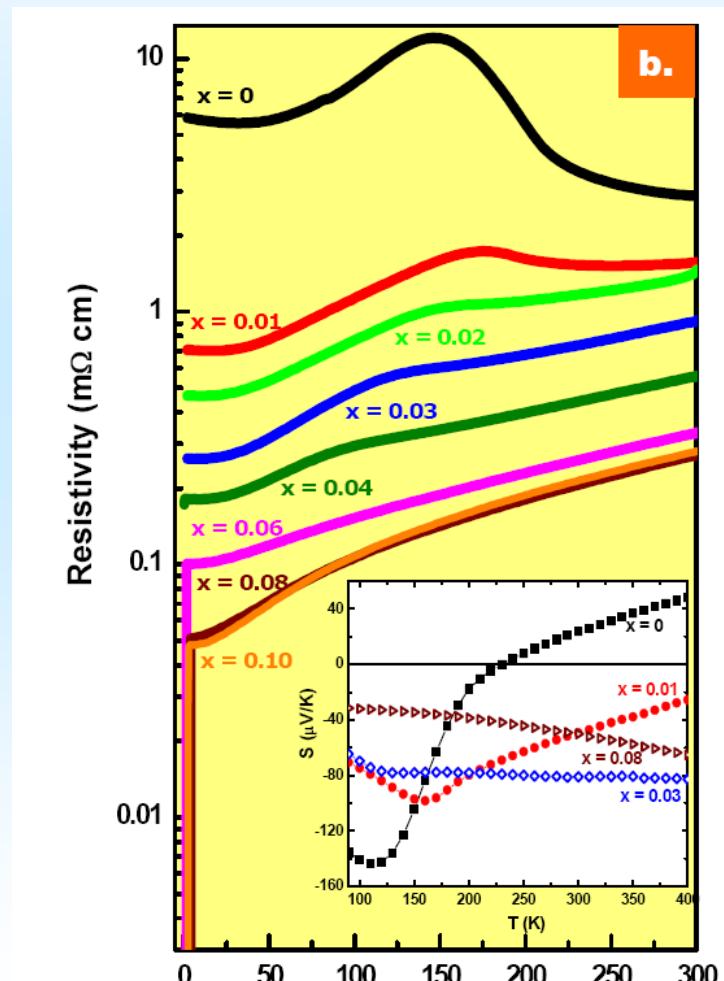
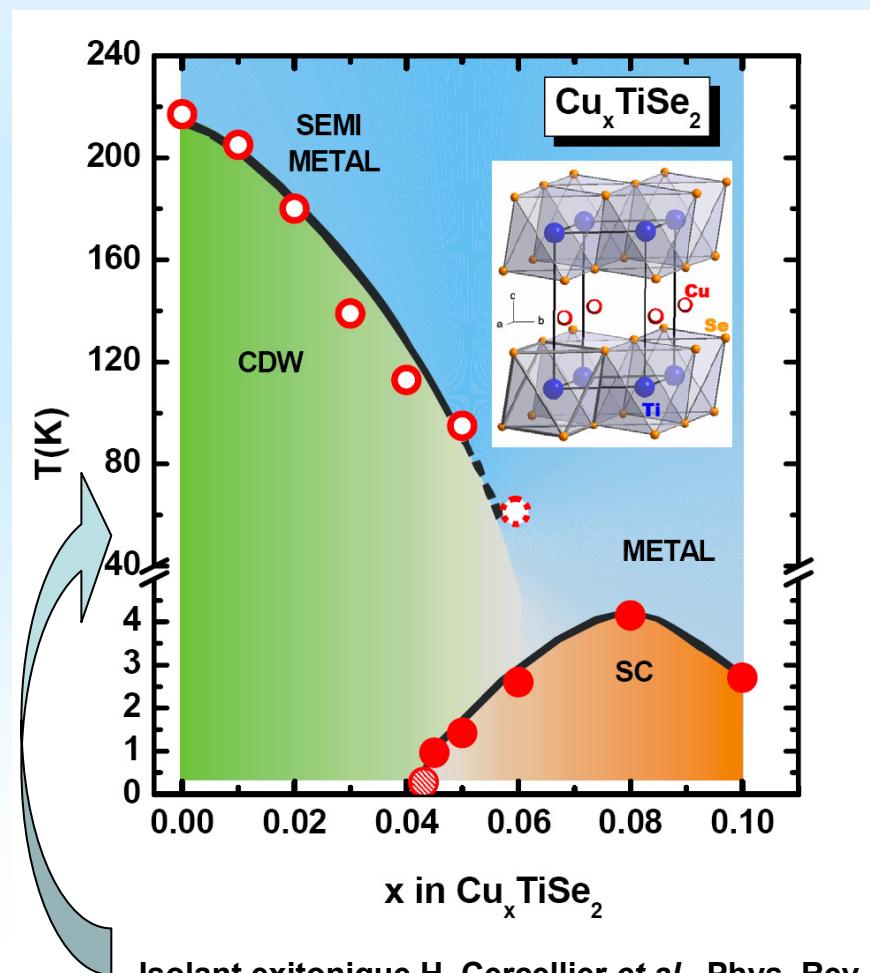
$TiSe_2$ $TiTe_2$
semi-Métaux

Energie



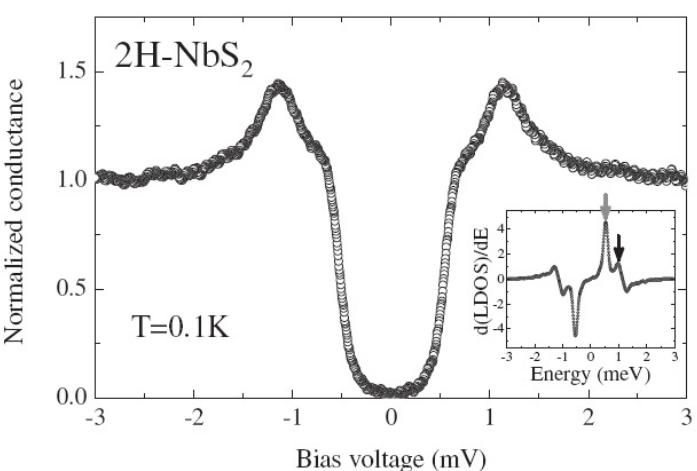
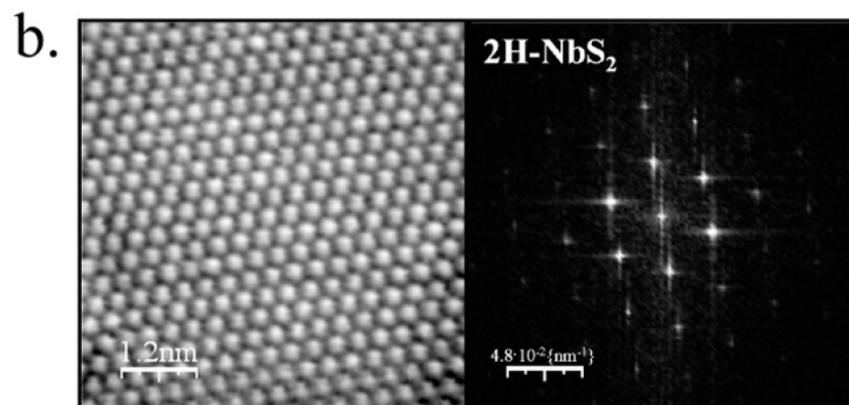
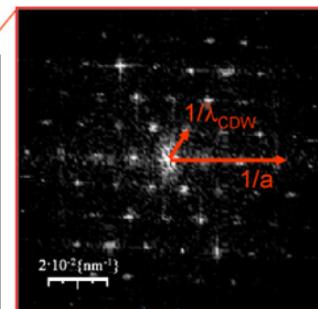
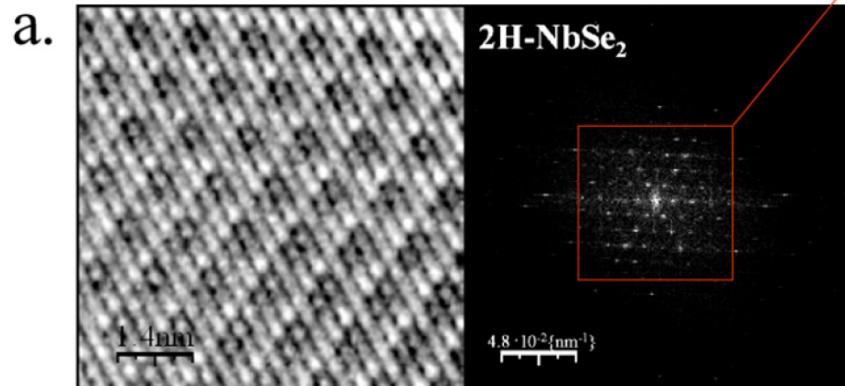
$TiSe_2$ ($X=S, Se, Te$) : Coexistence onde de densité de charges et supraconductivité

Cava et al. Nature Physics 2, 544 - 550 (2006)



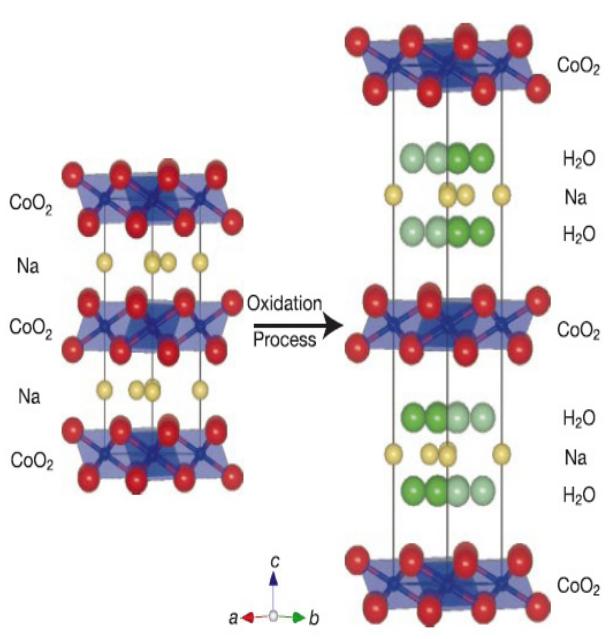
2H-NbX₂ (X=S, Se) : onde de densité de charges et supraconductivité non conventionnelle

STM



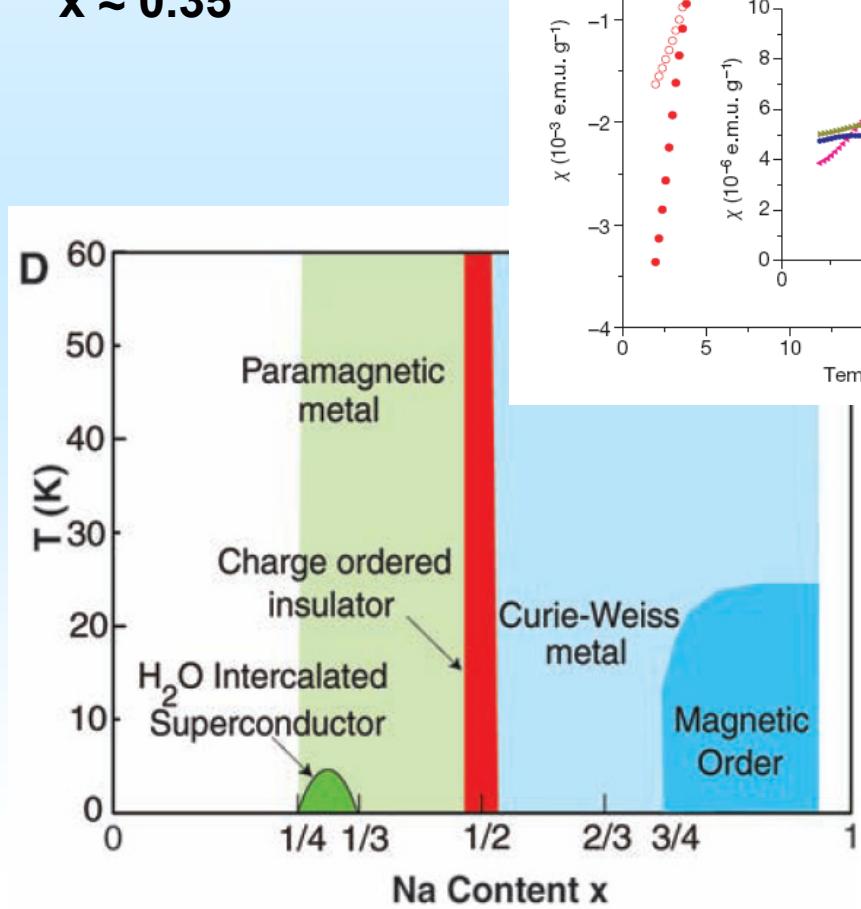
Supra à deux gaps ?

Des plans CdI_2 oxydes ? supraconductivité dans les cobaltates



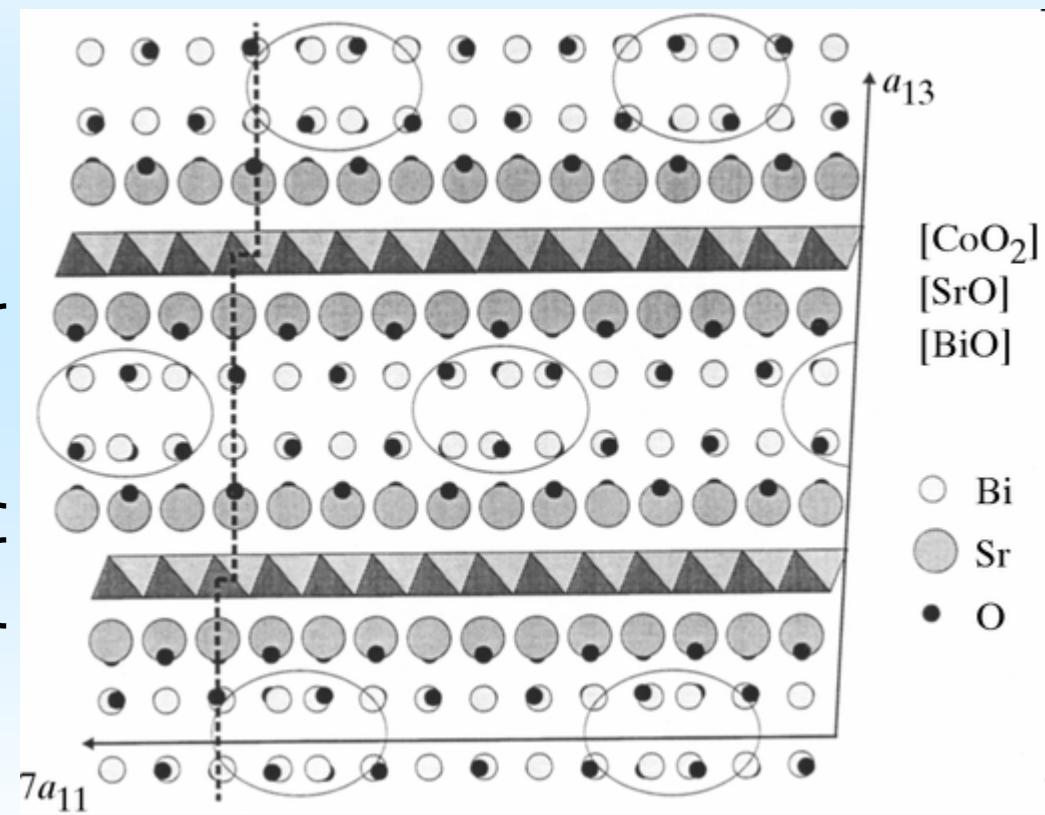
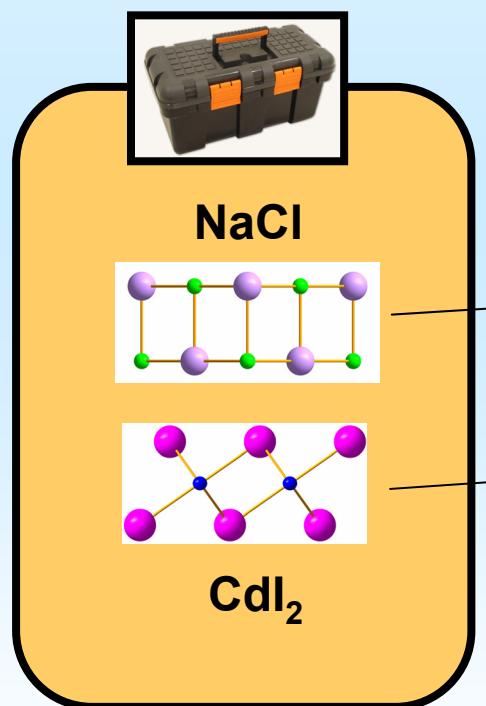
Superconductivity in two-dimensional CoO_2 layers

NATURE | VOL 422 | 6 MARCH 2003
 Kazunori Takada*, ‡, Hiroya Sakurai†, Eiji Takayama-Muromachi†,
 Fujio Izumi*, Ruben A. Dilanian* & Takayoshi Sasaki*‡



Plans CdI_2 et NaCl : phases misfits cobaltates

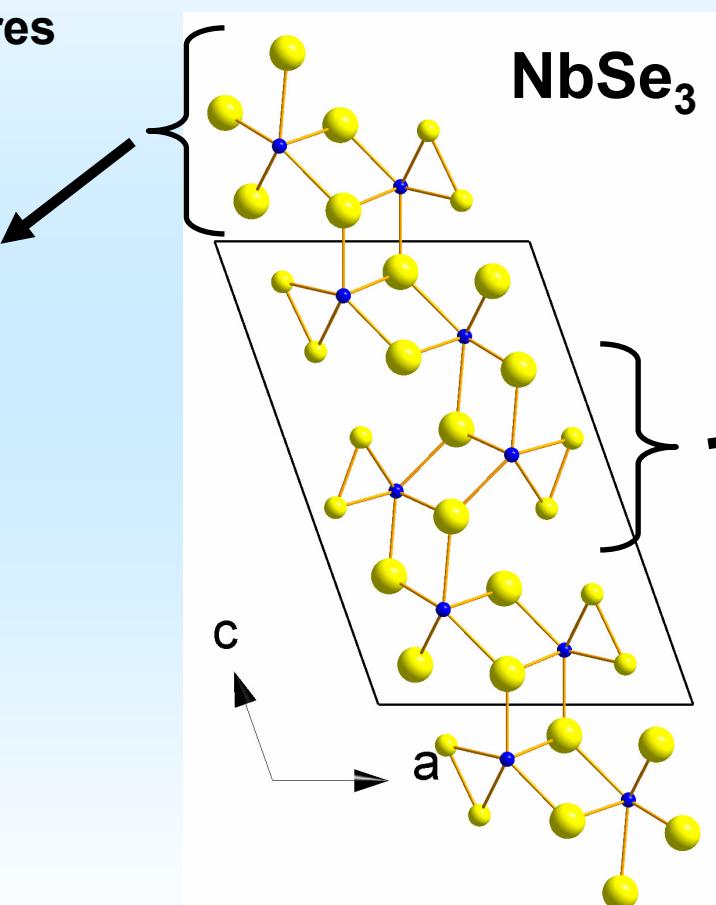
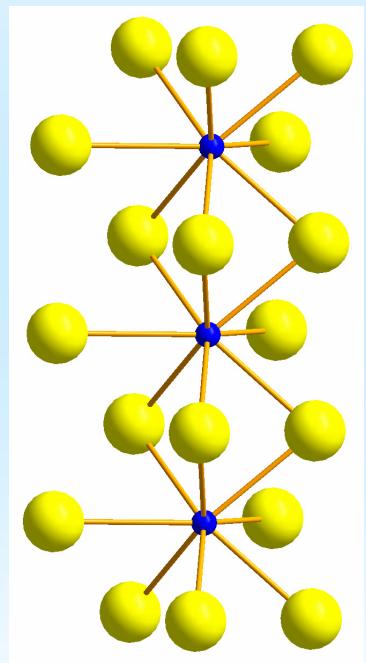
Intercroissance de feuillets types NaCl et CdI_2



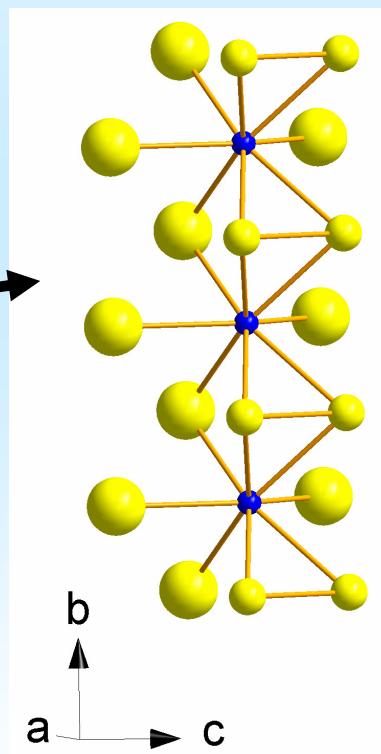
A five-dimensional structural investigation of the misfit layer compound $[\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82}$
Acta Cryst B (2000)
 H. Leligny, D. Grebille, O. Pérez, A. C. Masset, M. Hervieu and B. Raveau

Les phases 1D $NbSe_3$, TaS_3 et $(TaSe_4)_3I$: onde de densité de charges et non linéarités

Chaîne sans paires de soufre



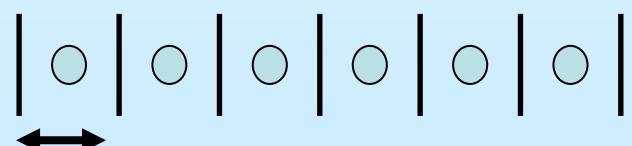
Chaîne avec paires De soufre



Chaines métalliques
bandes demi-remplies

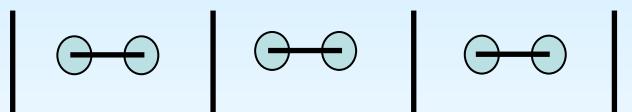
Onde de densité de charges et non linéarités

La chaîne métallique demie remplie :
instabilité de Peierls



a

Dimérisation



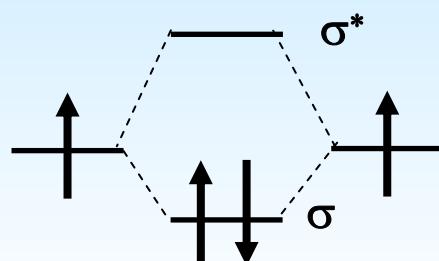
$2a$

Maille

1 orbitale
 $\frac{1}{2}$ remplie



2 Orbitales
 $\frac{1}{2}$ remplie



Formation
d'une orbitale
moléculaire

Solide

Métal

E_F

Isolant

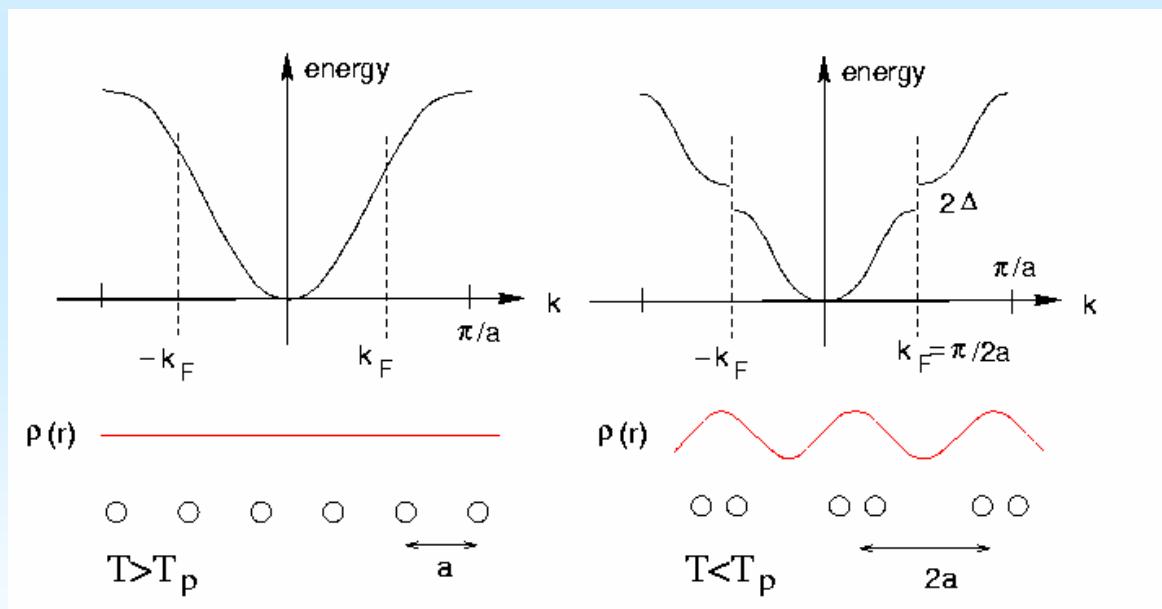
E_F

DOS

DOS

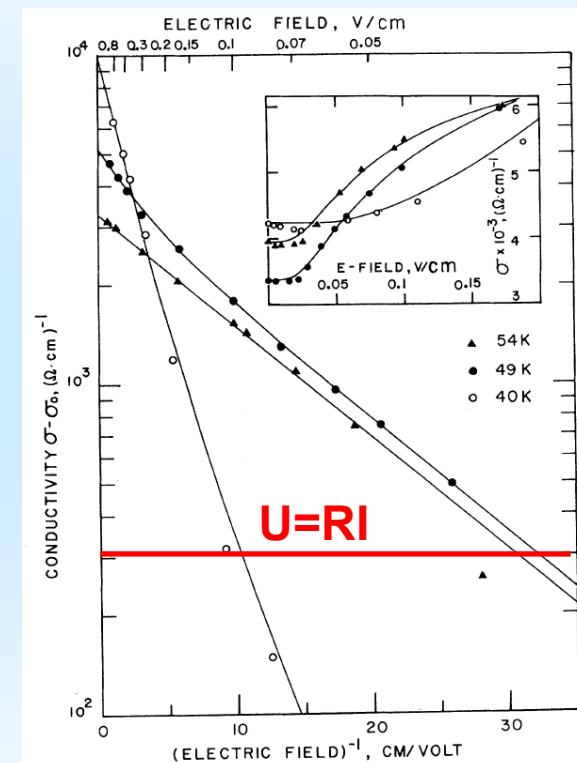
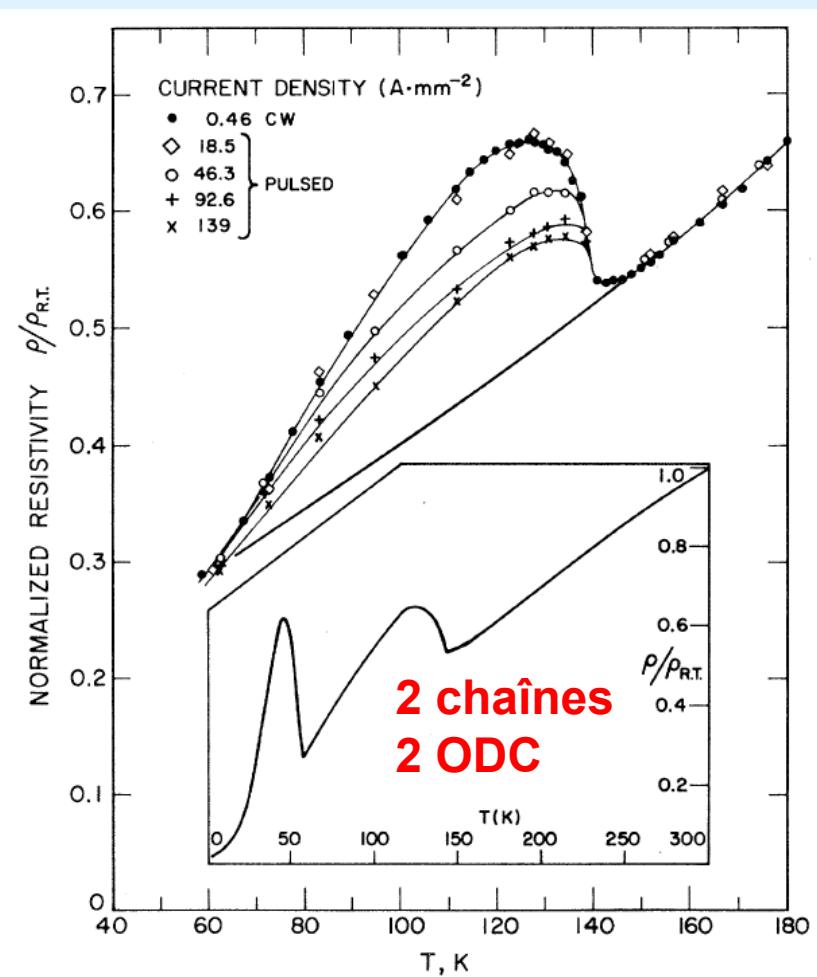
onde de densité de charges et non linéarités

La chaîne métallique demie remplie :
instabilité de Pierls



$NbSe_3$:

onde de densité de charges et non linéarités



Electric Field Breakdown of Charge-Density-Wave-Induced Anomalies in $NbSe_3$ †

P. Monceau,* N. P. Ong, and A. M. Portis
Department of Physics, University of California, Berkeley, California 94720

PRL 37, 602 (1976)

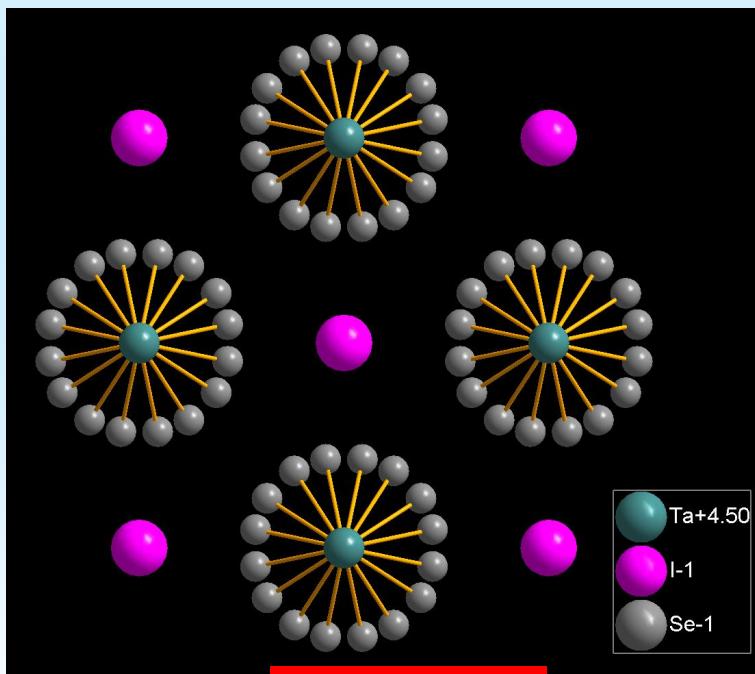
and

A. Meerschaut and J. Rouxel
Laboratoire de Chimie Minérale A, 44037 Nantes Cedex, France
(Received 1 June 1976)

Déviation à la loi d'Ohm
Décrochage de l'onde de densité de charge

Autres conducteurs unidimensionnels ...

Composés inorganiques quasi-1D :
TaS₃, (TaSe₄)₂I



(TaSe₄)₂I

P. Gressier, L. Guemas, A. Meerschaut,
Acta Cryst. B 38 (1982) 2877

Collaboration
 IMN – CRTBT

Phases 1D oxydes à ODC : Bronzes de Molybdène K_{0.3}MoO₃ ... voir livre Claire Schlenker
 low dimensional electronic properties of molybdenum bronzes and oxides.

Conclusion

- *Les grandes classes de composés ont des structures dérivant d'empilements simples*
- *Il existe une relation étroite entre la structure et les propriétés*
- *Des propriétés remarquables naissent :*
 - à la proximité de la transition isolant métal de Mott
 - dans les composés magnétiques ou métalliques de basse dimensionnalité



Composés à propriétés électroniques remarquables

2. recherche de nouveaux composés

Laurent Cario

Institut des Matériaux Jean Rouxel, Nantes (France)

Laurent.cario@cnrs-imn.fr

Plan

Partie 1 : Structures et propriétés des grandes classes de composés connus

- 1. principaux types structuraux**
- 2. Oxydes de métaux de transition**
- 3. Chalcogénures de métaux de transition**

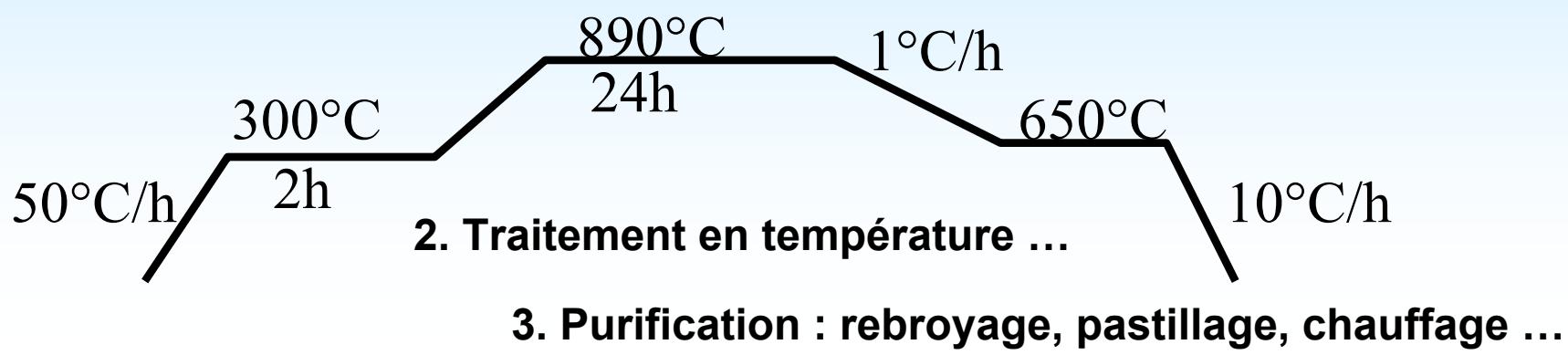
Partie 2 : Recherche de nouveaux composés inorganiques

- 1. Synthèse et recherche exploratoire de nouveaux composés**
- 2. Outils de rationalisation en chimie inorganique**
- 3. Conception raisonnée de nouveaux composés inorganiques**

Comment synthétiser une céramique ?

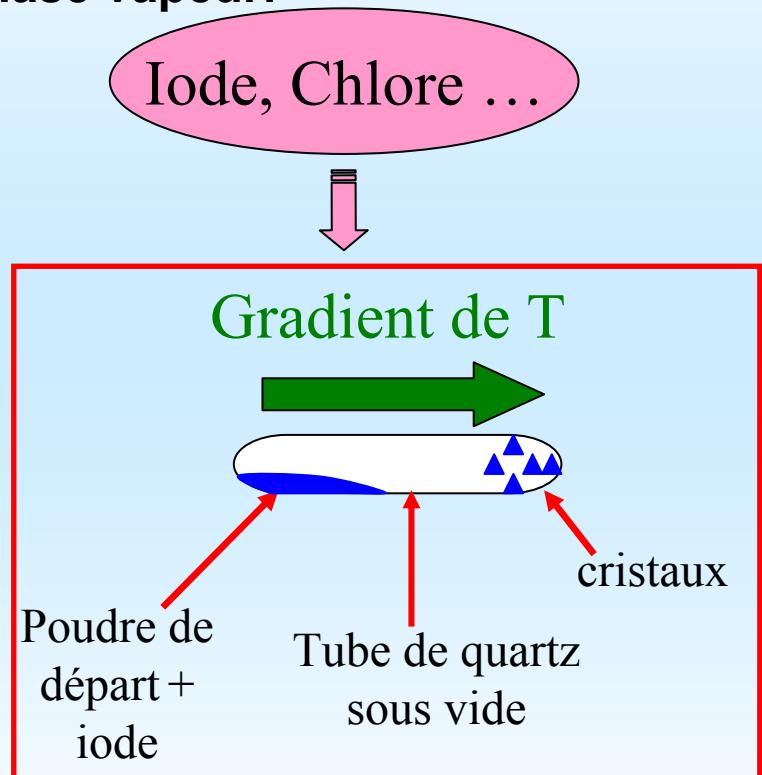
Synthèse par voie haute température

1. Mélange des précurseurs : éléments, composés binaires ...



Comment faire croître des cristaux ?

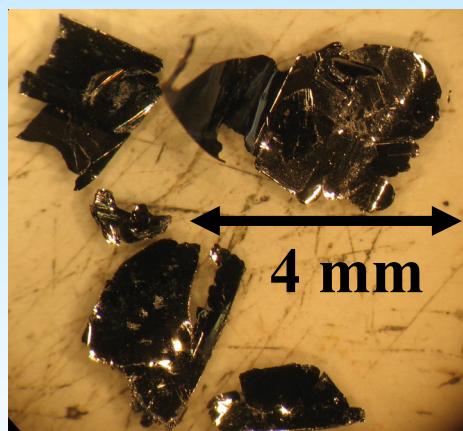
1. Méthode de transport en phase vapeur:



Cristaux de TiSe_2 @ S. Salmon



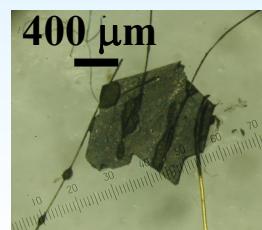
Cristaux de $(\text{LaS})_{1.193}\text{VS}_2$



2. Méthode des flux :

Croissance dans un bain solubilisant partiellement le composé

Ex : LiVO_2 (flux LiBO_2) : valence V3+ \Rightarrow stable pour $p\text{O}_2 \approx 10-20$ atm vers 850°C

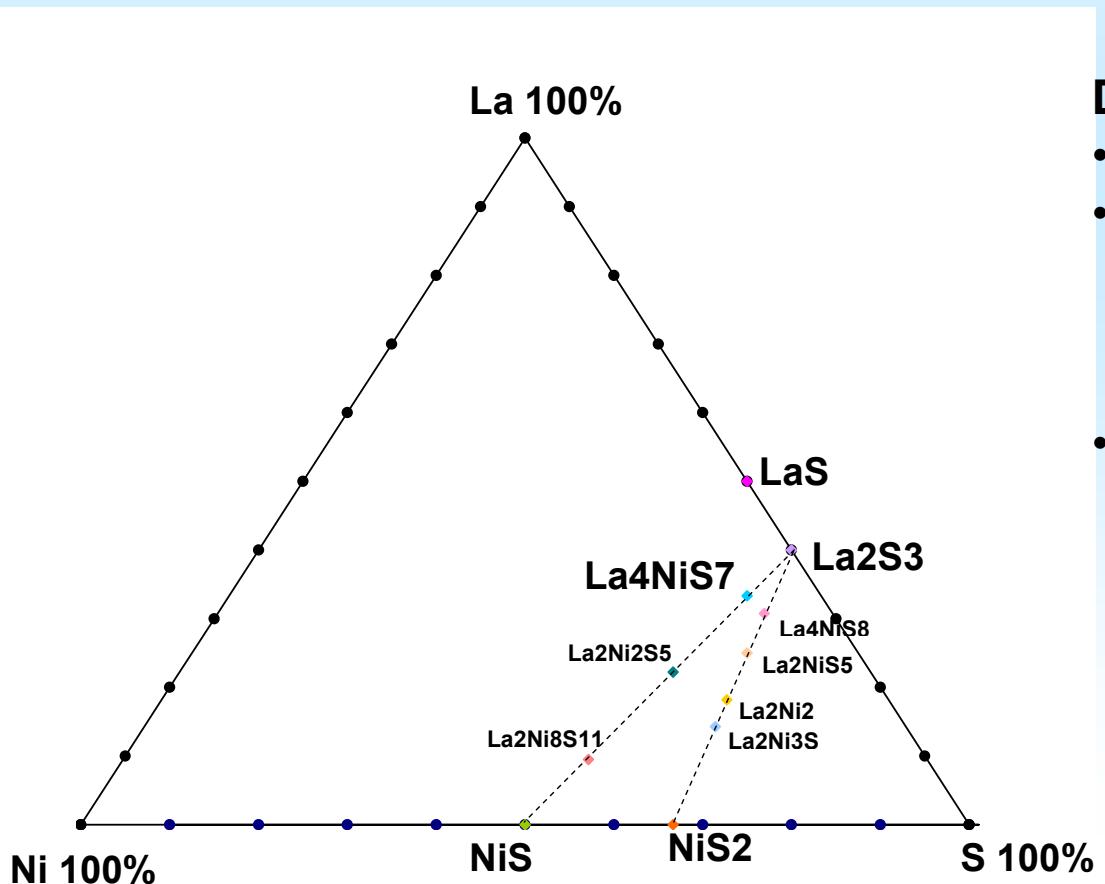


Comment faire des nouveaux composés ?

1 – exploration systématique

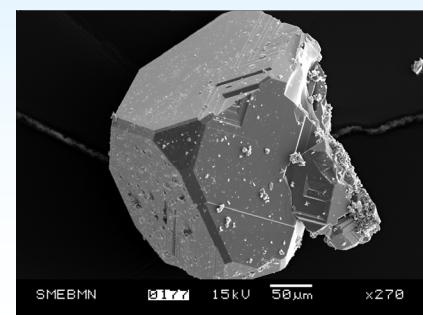
Pour composés ternaires :

Espace des compositions à 3 dimensions
+ choix de la température de synthèse



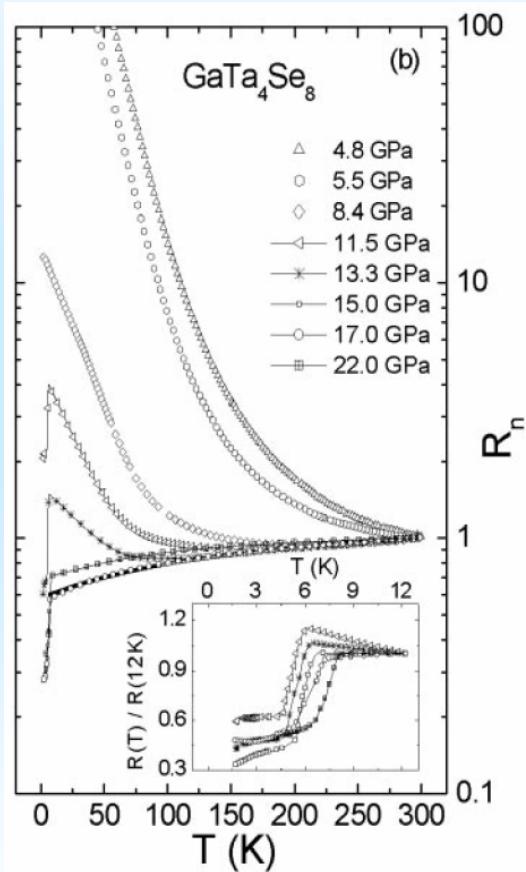
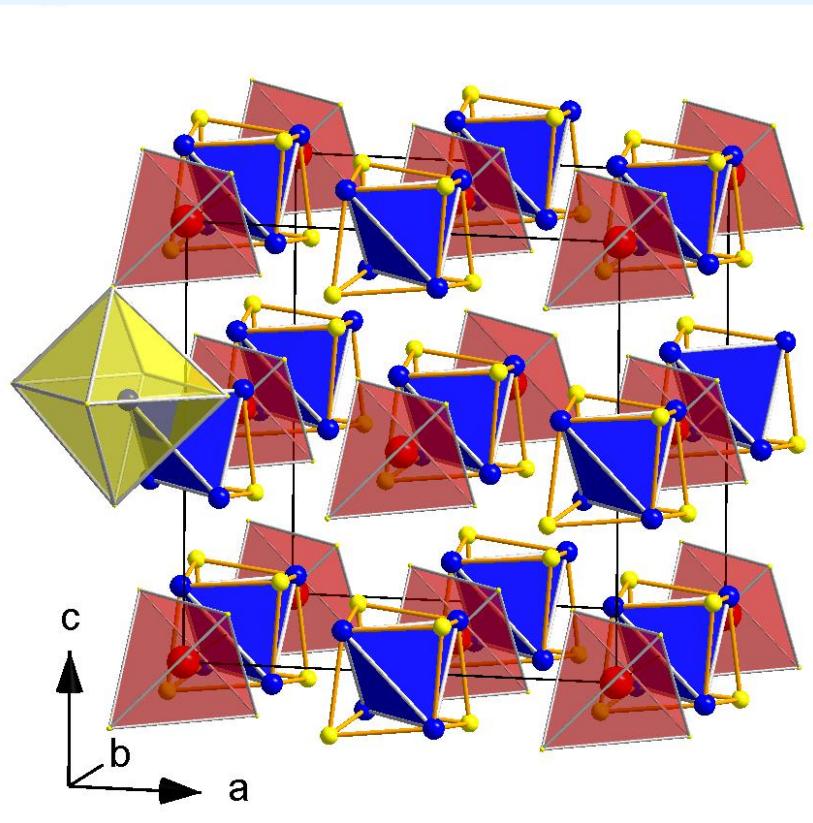
Démarche :

- Synthèse
- détection de phases nouvelles :
 - DRX,
 - Analyses chimiques (SEM)
 - MET
- Synthèse de cristaux des phases repérées : étude structurale



Comment faire des nouveaux composés ?

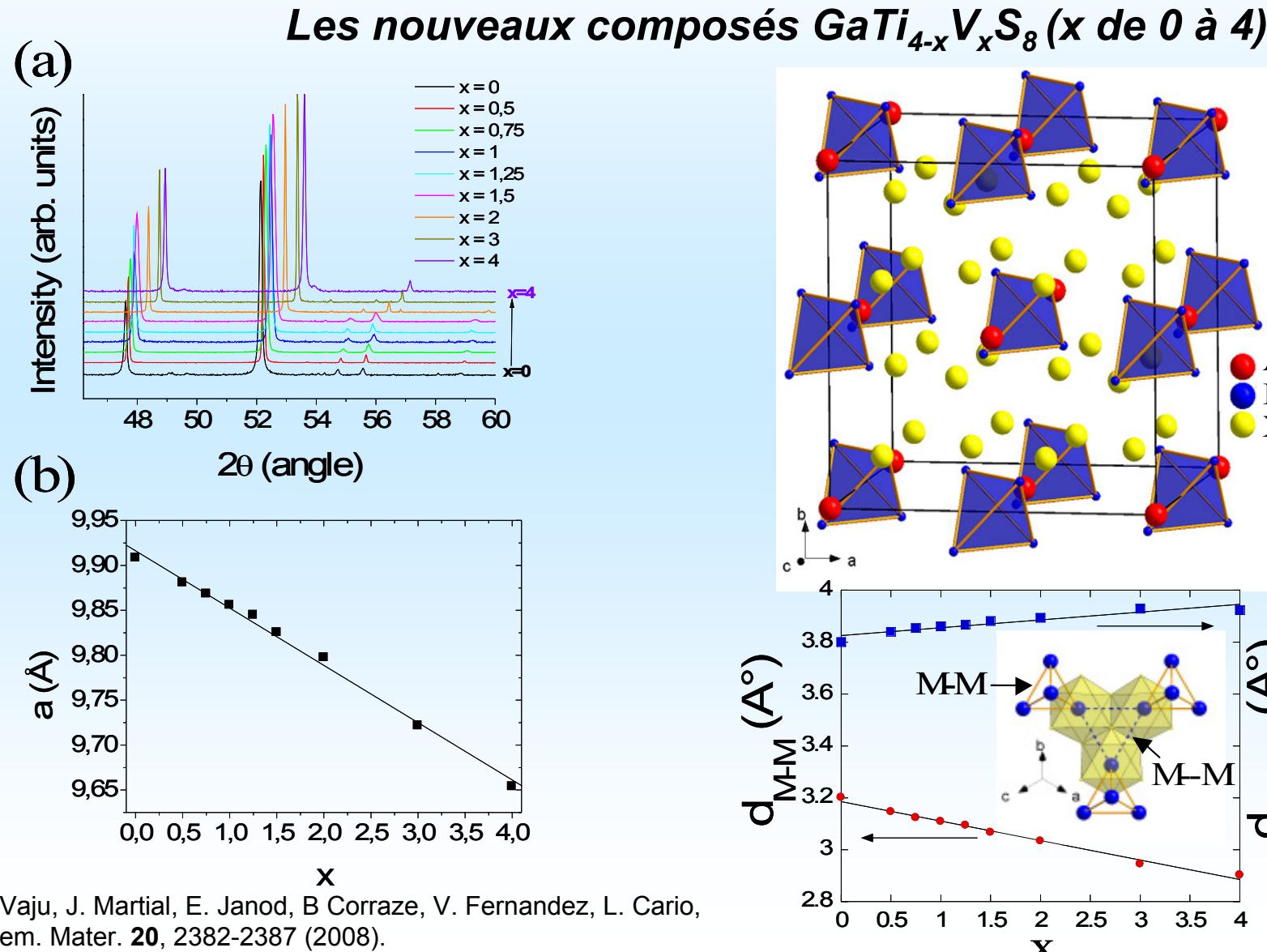
2 – exploration ciblée



Abd-Elmeguid et al.
Phys. Rev. Lett.
93, 126403 (2004)

AM_4X_8 : isolants de Mott
"fragiles" Gap ~ 0.2 eV

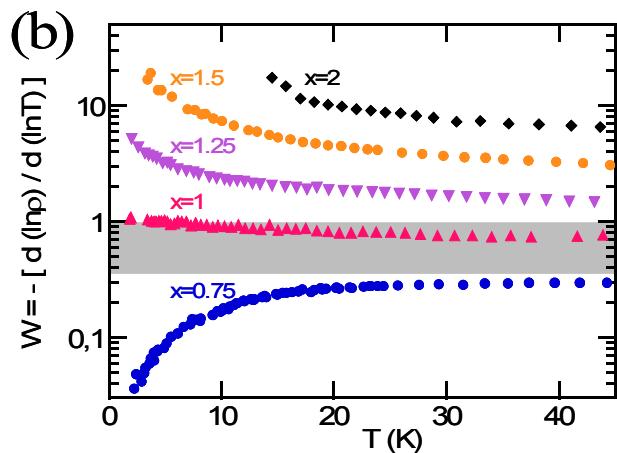
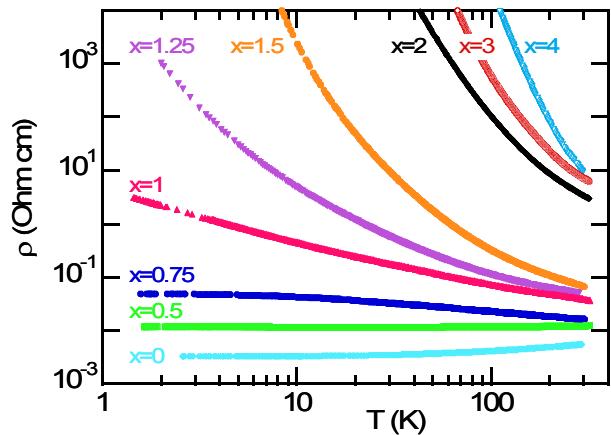
Exploration ciblée : recherche TMI dans AM_4X_8



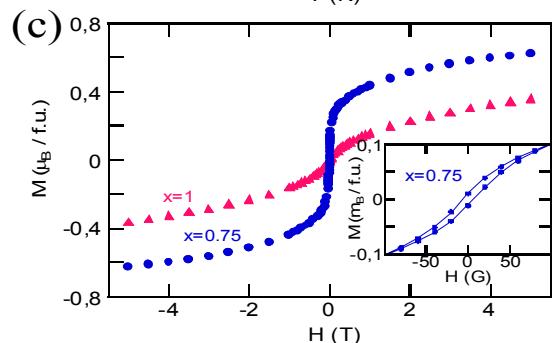
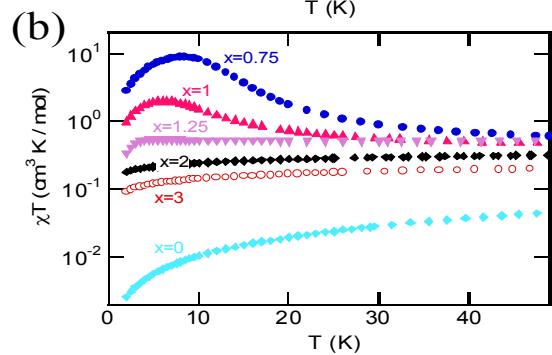
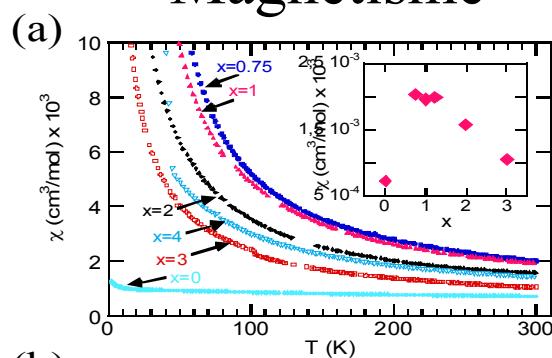
Recherche de nouvelles propriétés

Transition Isolant Métal liée au désordre apparition de ferromagnétisme

Résistivité



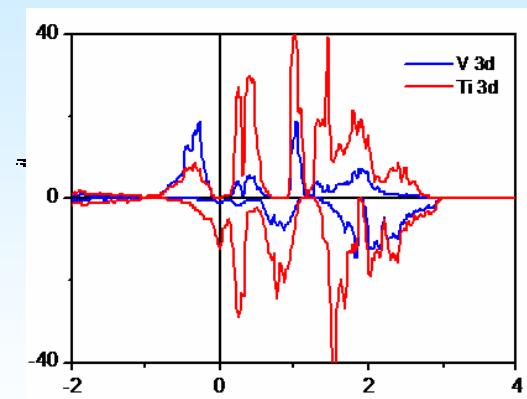
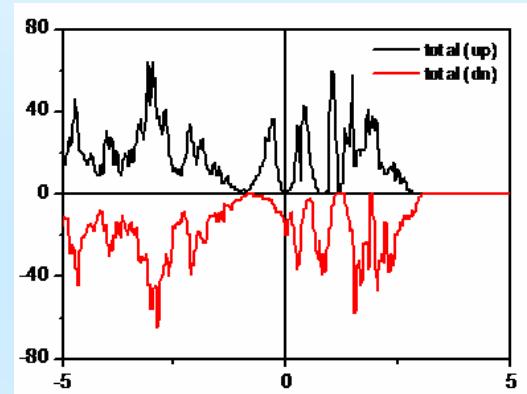
Magnétisme



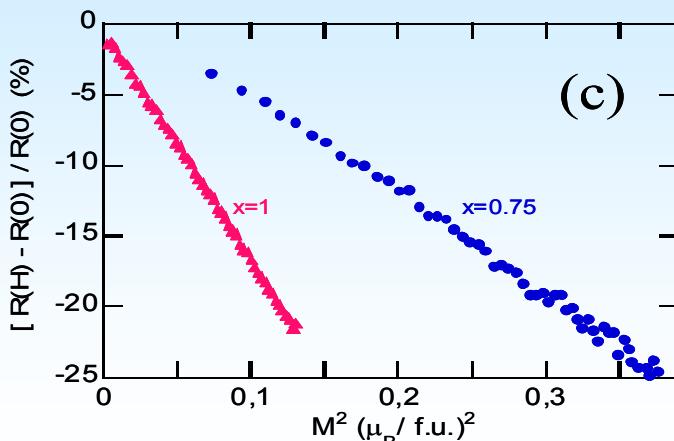
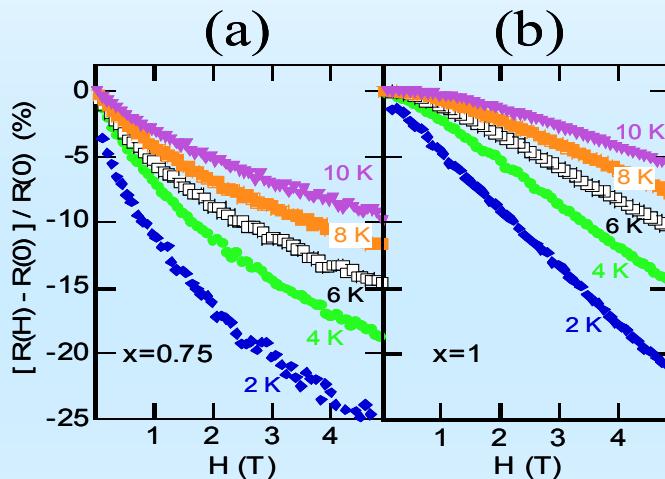
Recherche de nouvelles propriétés

Demi-métal ferromagnétique et magnétorésistance négative

Calcul de structure de bandes

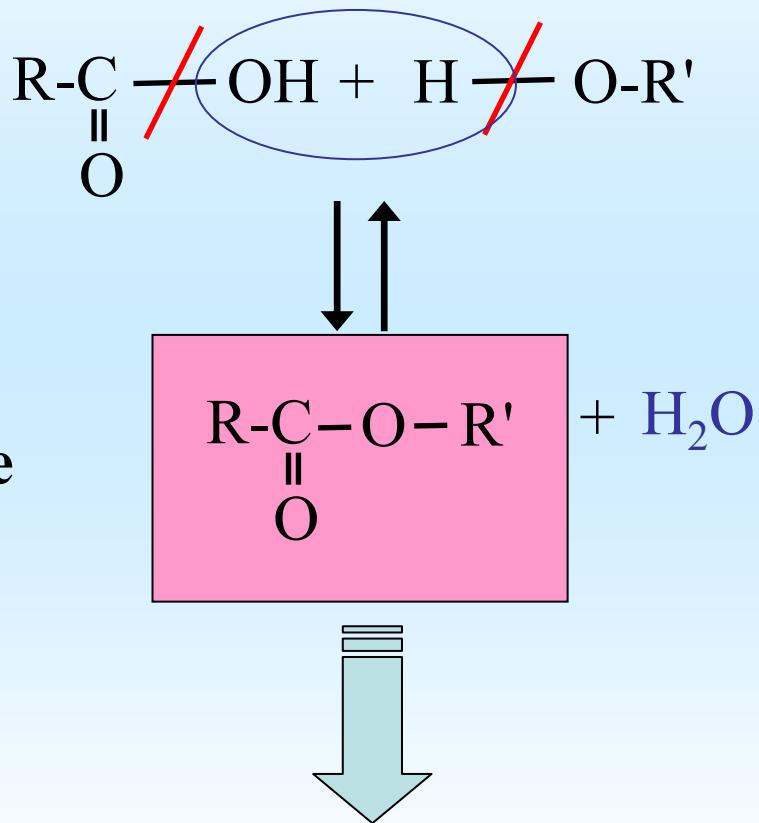


Magnétorésistance



Nouveaux composés organiques : conception et rétro-synthèse

Rétro-synthèse



Contrôle de la structure

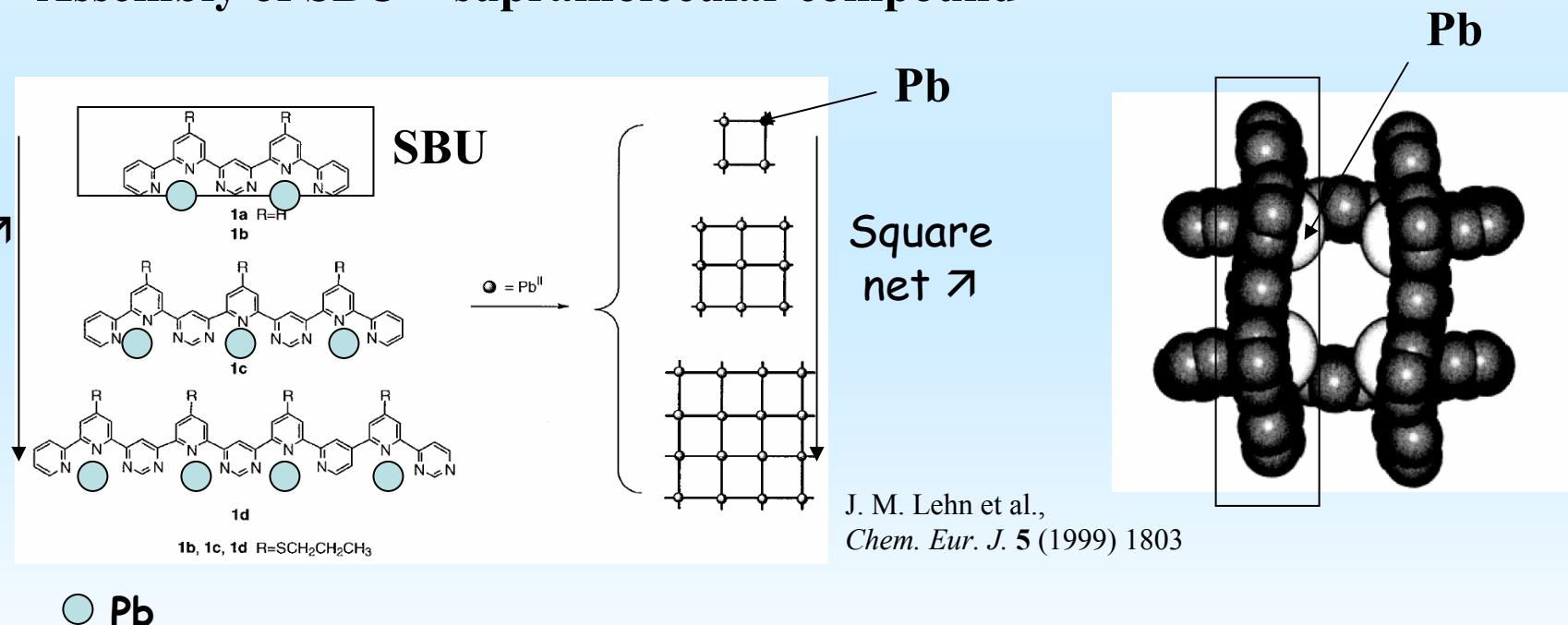
Contrôle des propriétés

Fonctionnalisation

Composés supramoléculaires et concept de SBU

« SBU » Secondary Building Units

Assembly of SBU = supramolecular compound

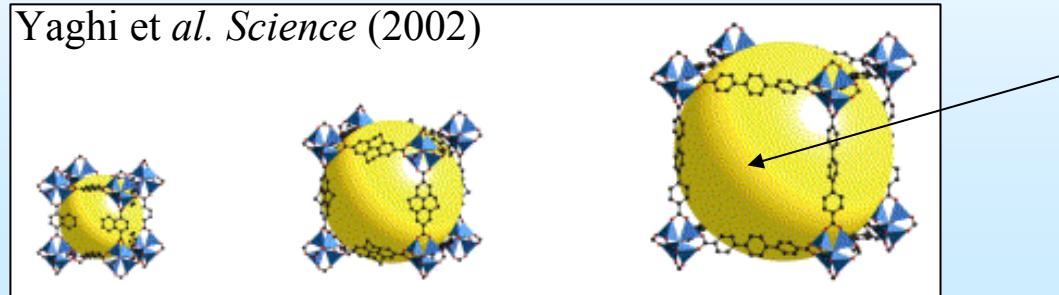


Supramolecular compounds can be designed by auto-assembling Secondary Building Units (SBU).

Composés hybrides : liés des SBU inorganiques

- « *MOF* » METAL OXIDE FRAMEWORK compounds

Yaghi et al. *Science* (2002)

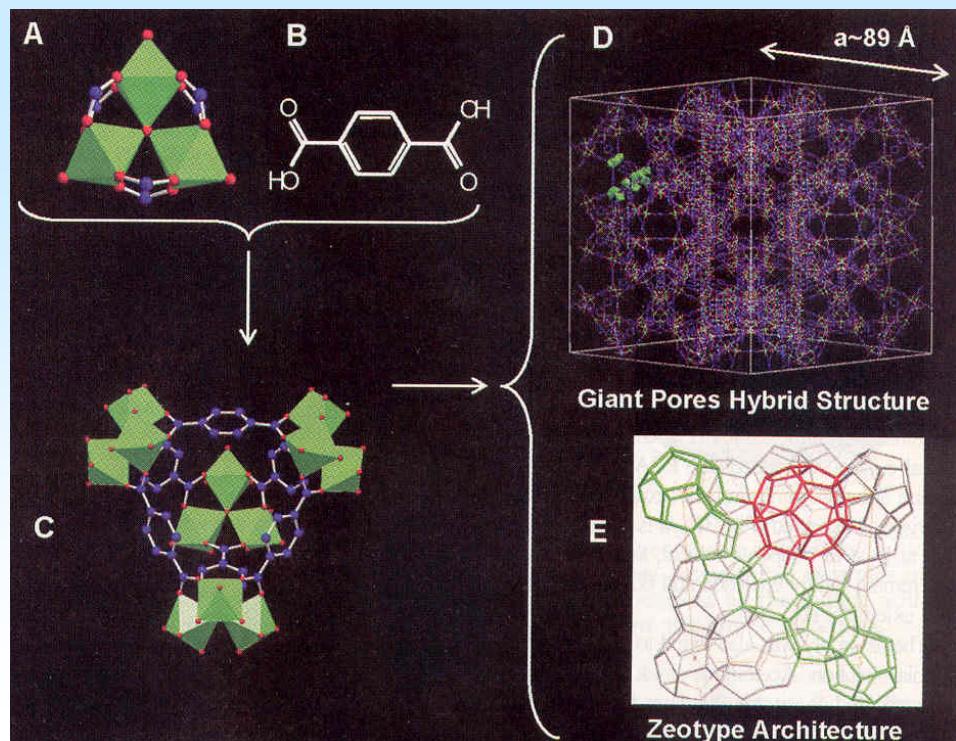


Pore size tuned with the organic linker

- « *MOF* » with giant pores

→ MIL101

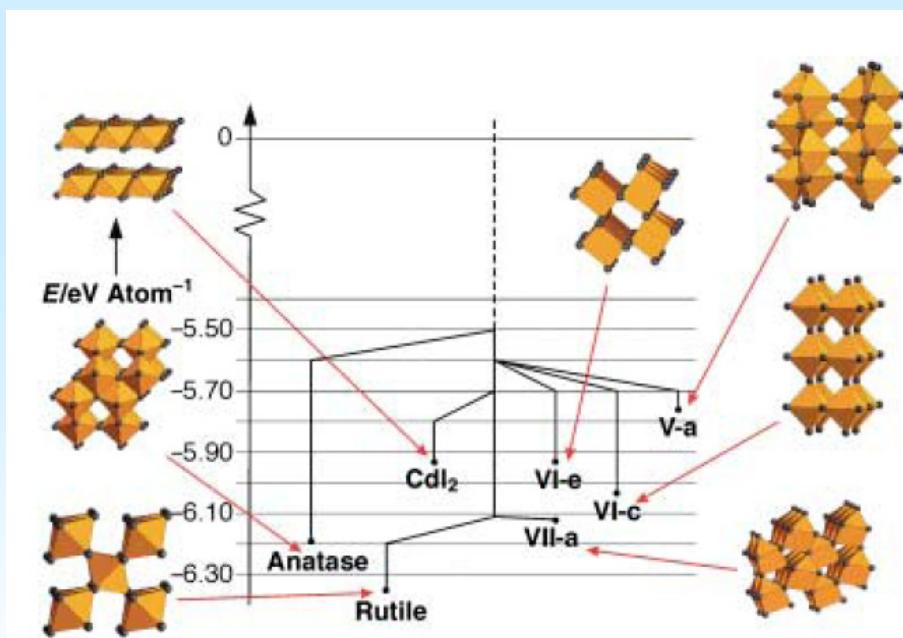
Férey et al. *Science* (2005)



Composés inorganiques

1- prédition des structures

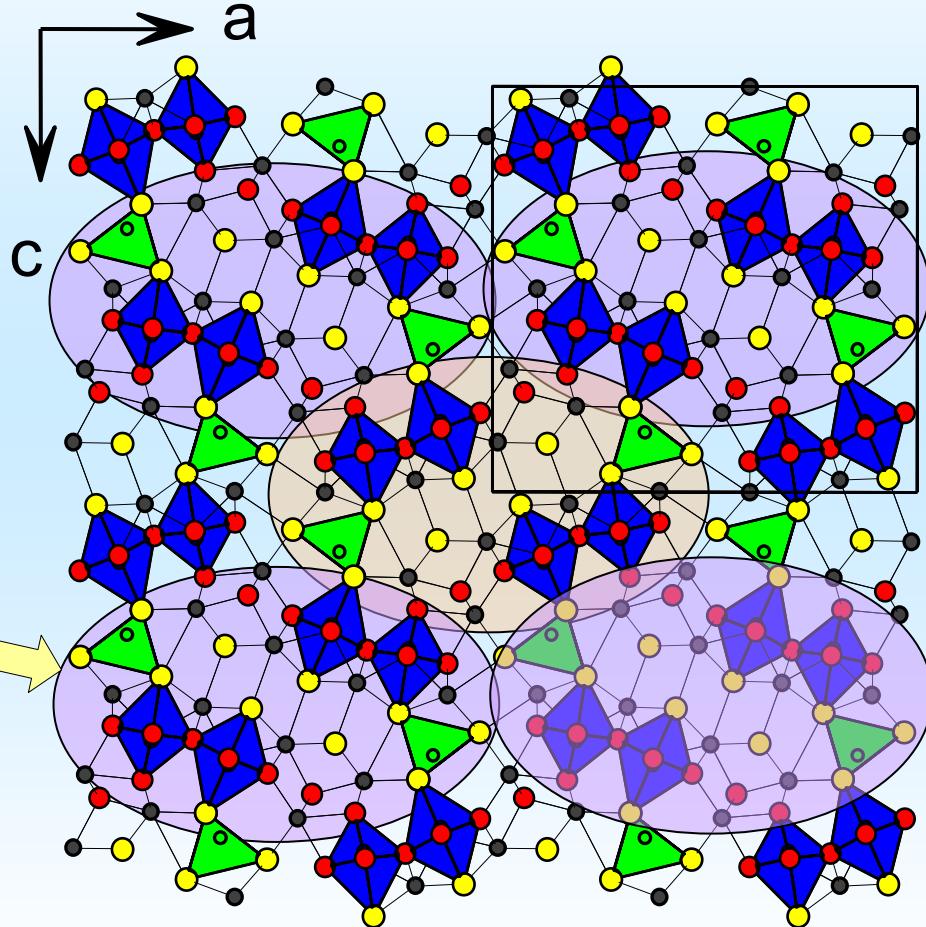
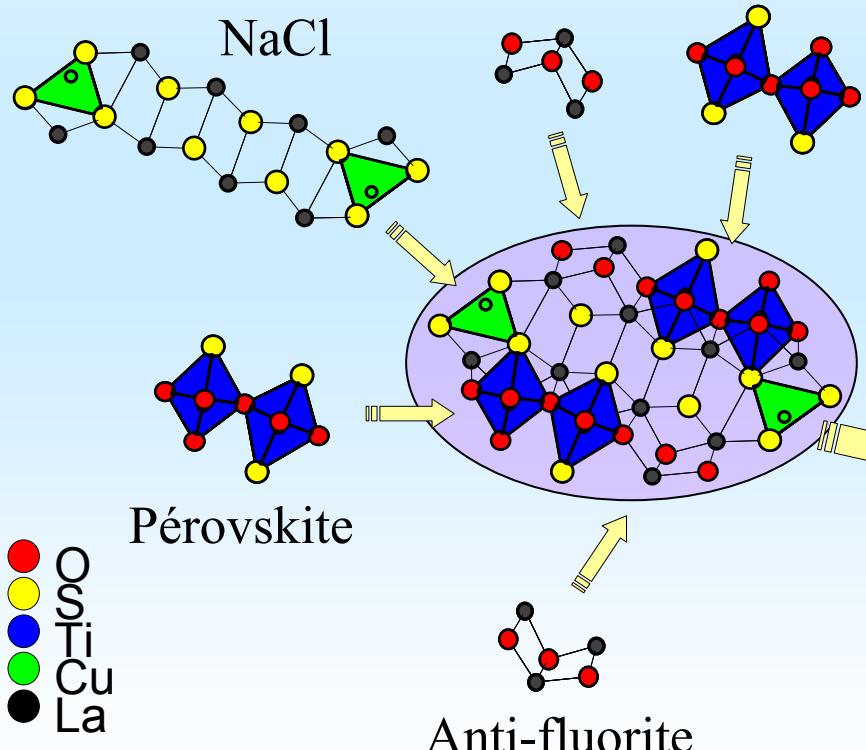
Exploration of the energy landscape of MgF_2



J. C. Schoen and M. Jansen, *Angew. Chem. Int. Ed.* **35** (1996) 1286 ;
M. Jansen, *Angew. chem. Int. Ed.* **41** (2002) 3746.

Composés inorganiques

2 – description modulaire et série d'homologues

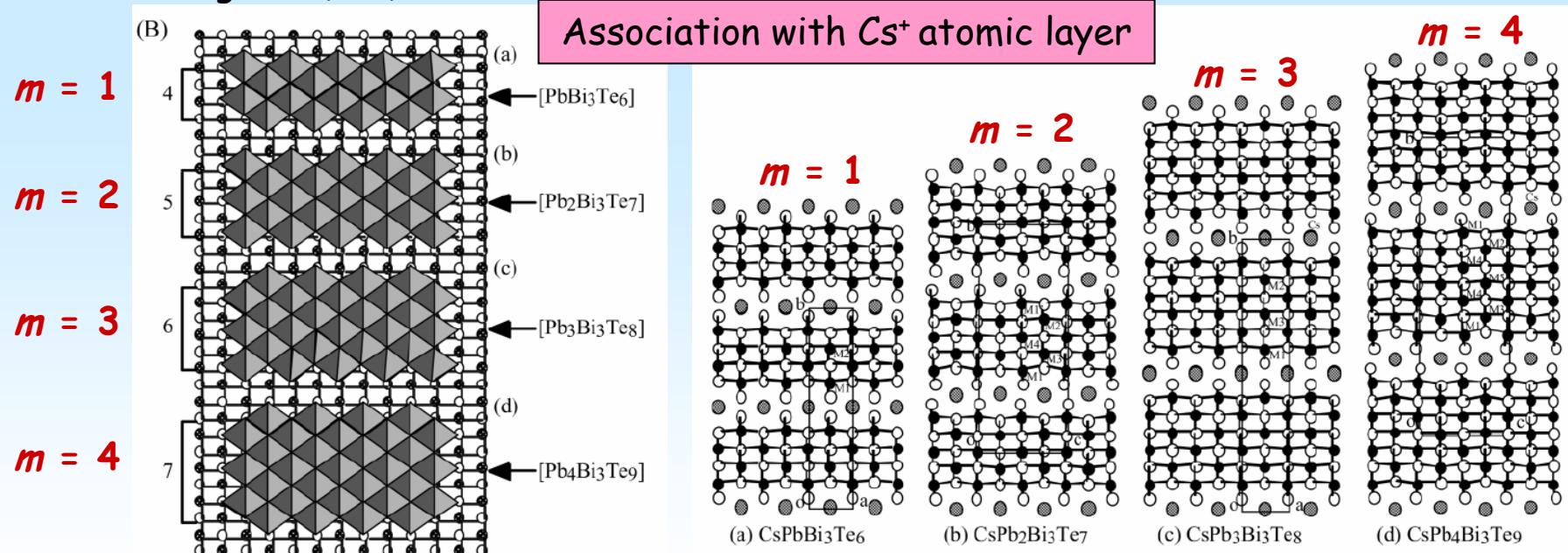


Composés inorganiques

2 – description modulaire et série d'homologues

homologous series $CsPb_mBi_3Te_{5+m}$
 Obtained from PbTe type modules

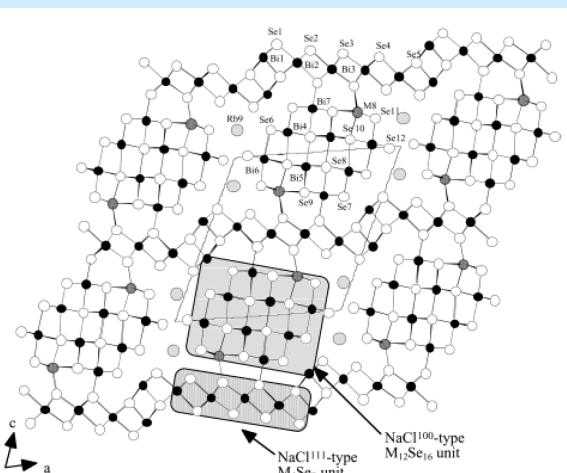
PbTe structure (NaCl type)
 along the (110) direction



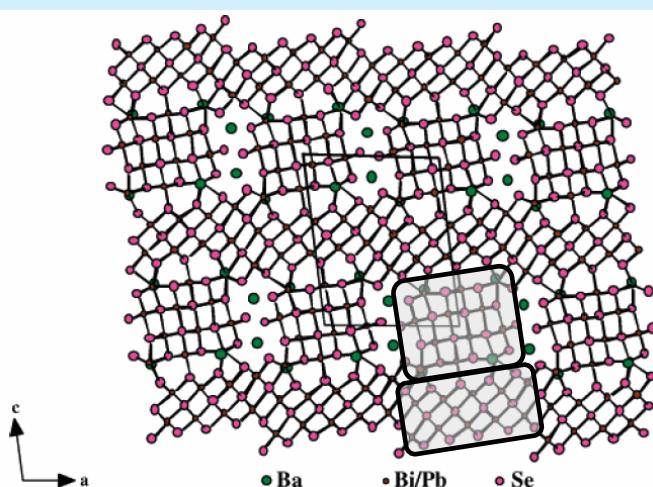
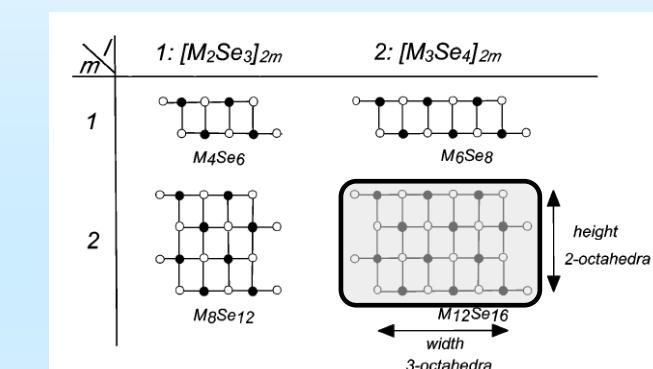
Composés inorganiques

2 – description modulaire et série d'homologues

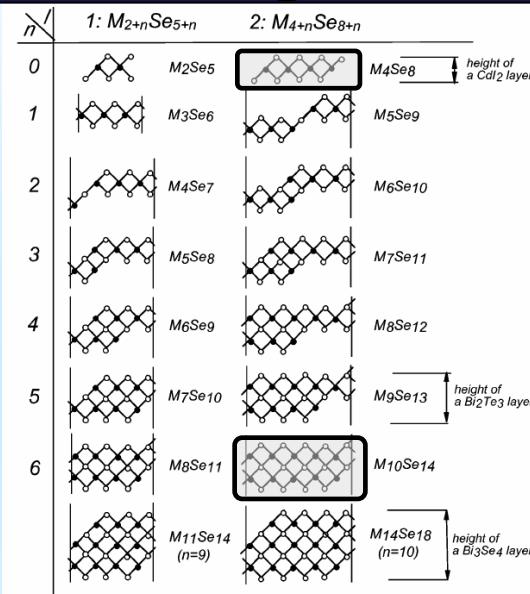
Megaséries $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$



$\text{RbSnBi}_7\text{Se}_{12}$ ($m=2$, $l=2$, $n=0$)



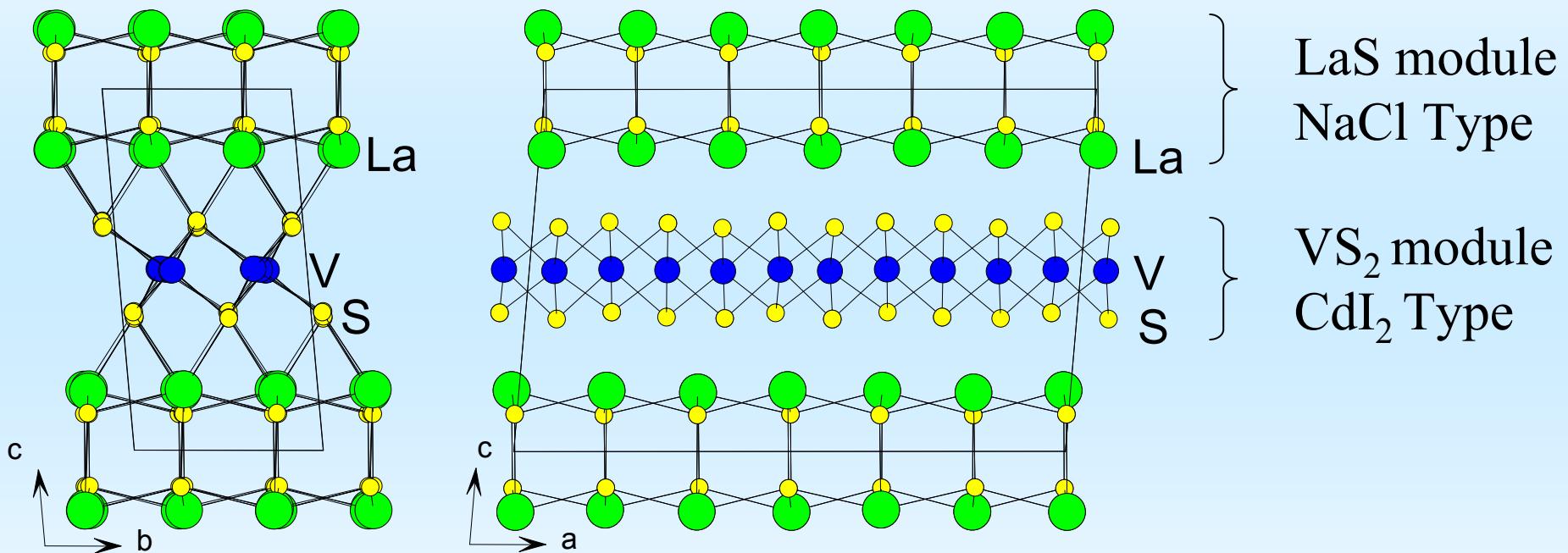
$\text{Ba}_{2+x}\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{15}$ ($l=2$, $m=2$, $n=6$).



A. Mrotzek and M. G. Kanatzidis,
Acc. Chem. Res. **36** (2003) 111.

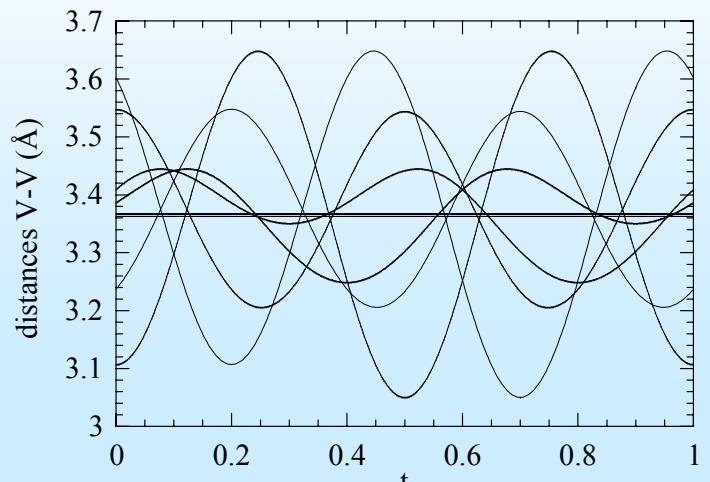
La série d'homologues misfits 2D :

Structure incommensurable de $(LaS)_{1.196}VS_2$

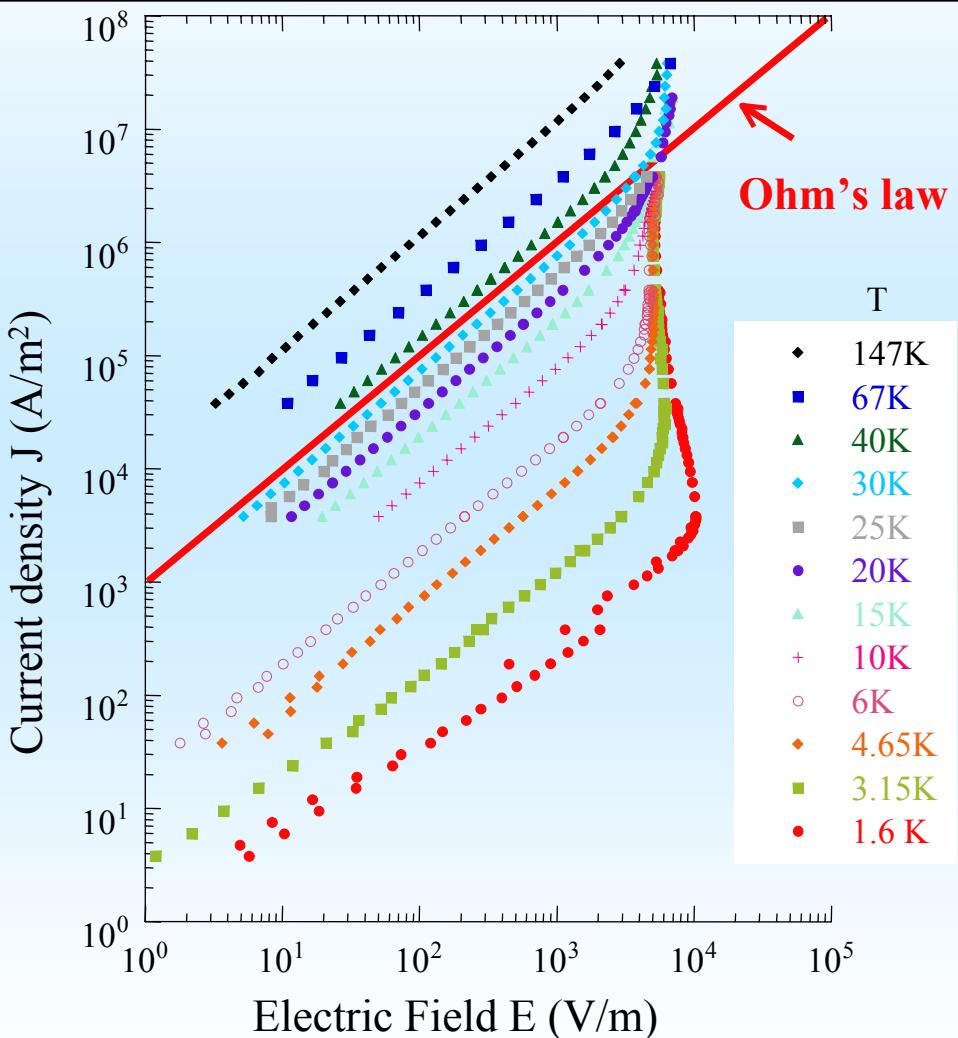
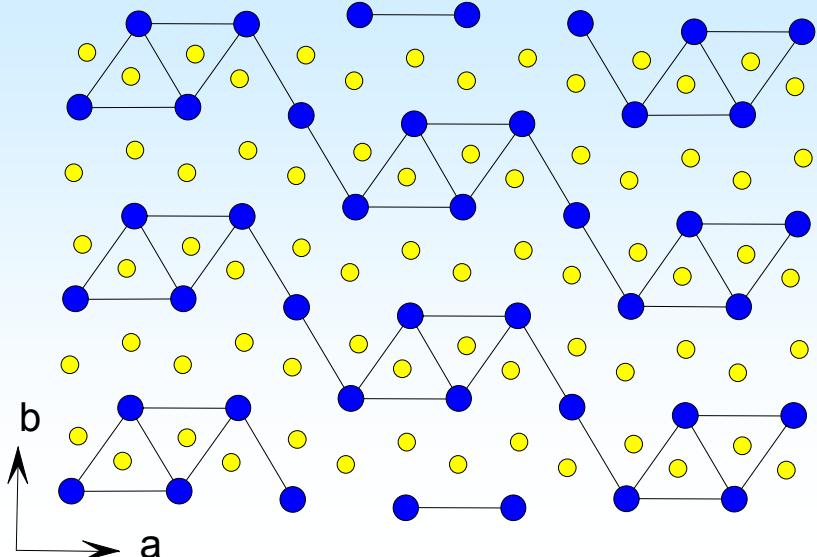


Triclinic (3+1)D Superspace Group $X\bar{1}(\alpha\beta\gamma)$ with pseudo C centering

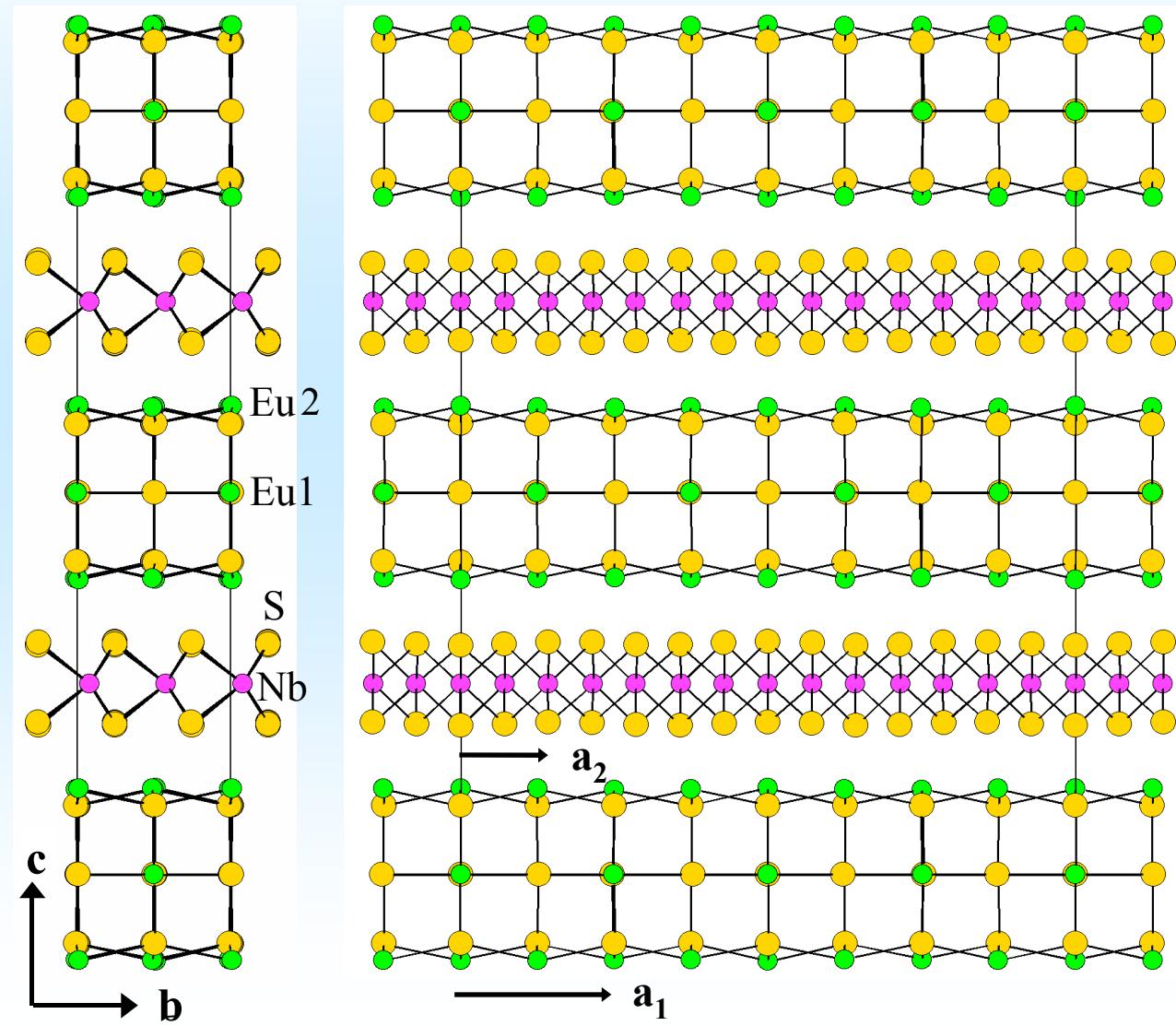
Modulation des distances V-V et non linéarités



Strong V-V distance modulation



$[(\text{EuS})_{1,5}\text{I}]_{1,15}\text{NbS}_2$: module NaCl à 3 plans atomiques



(3+1)D Superspace Group
 $Xm\bar{2}m(\alpha 00)$
with pseudo F centering

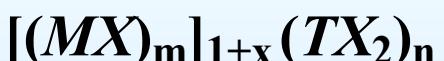
} EuS module
3 atomic layers

} NbS₂ module

L. Cario, A. Lafond, P.
Palvadeau, C. Deudon,
and A. Meerschaut,
J. Sol. St. Chem., **147**, 58, 1999.

Les phases misfits : série d'homologues 2D

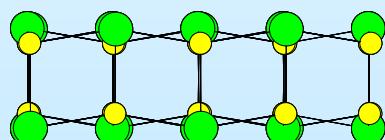
A. Meerschaut (ed.),
Materials Science Forum, 100-101 (1992)



M = Sn, Sb, Pb, Bi, Rare Earths
T = Ti, V, Cr, Nb, Ta ; X = S, Se

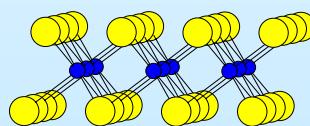
Or

2D Modules

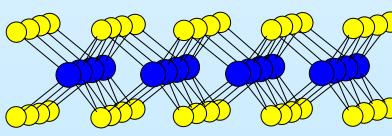


• M • X

$MX = Q$



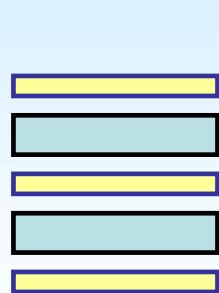
• T (Ti, V, Cr)



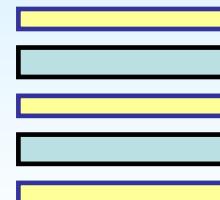
• T (Nb, Ta)

$TX_2 = H$

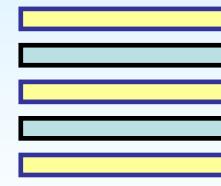
Different sequence types mQ/nH $m = 1, 1.5, 2$ and $n = 1, 2$ or 3



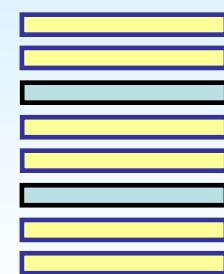
2Q/1H



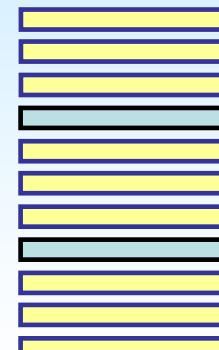
1.5Q/1H



1Q/1H

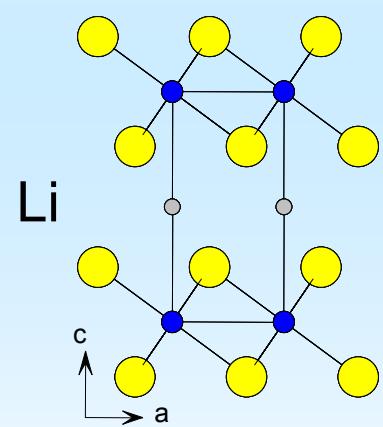


1Q/2H

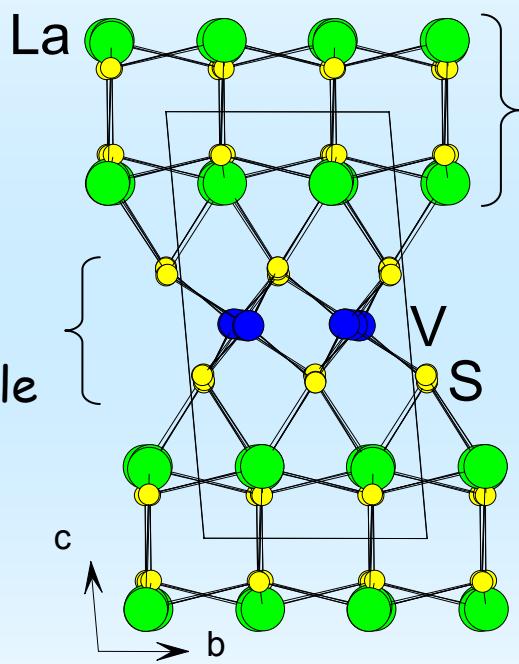


1Q/3H

Modules 2D et environnements chimiques



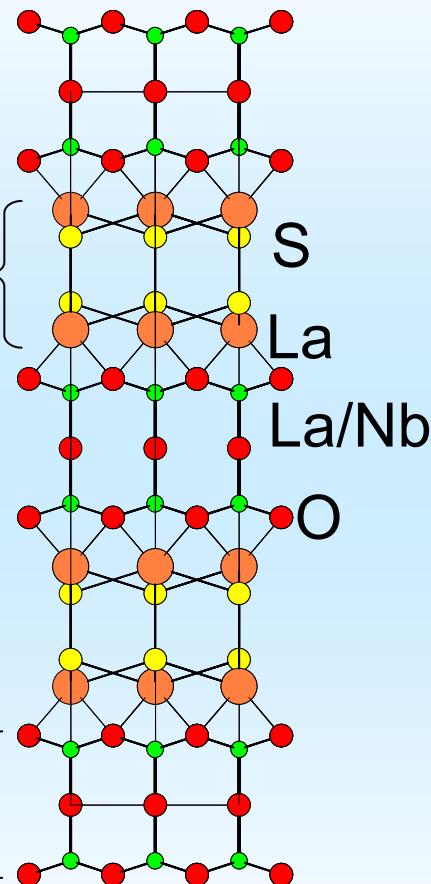
van Laar, B. Ijdo, D.J.W.
JSSC 1971



L. Cario et al.
Mater. Res. Bul. 40 (2005) 125

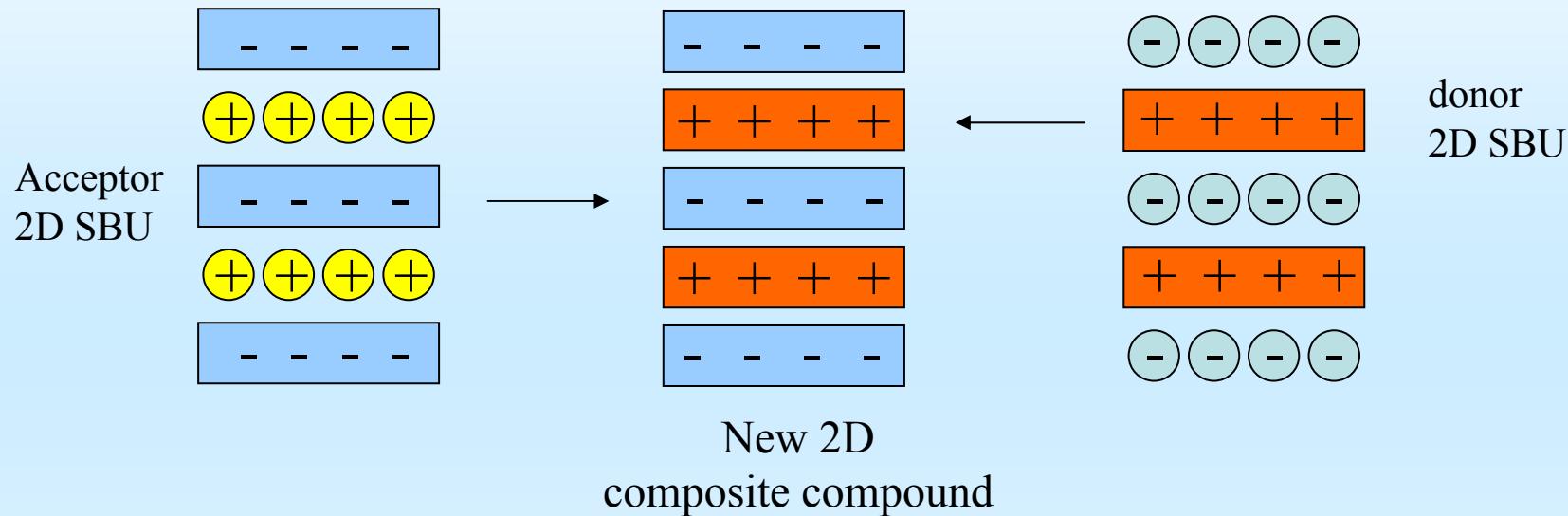
RES
Rock salt
type module

LaNbO_5
Perovskite
type module



L. Cario et al.
Inorg. Chem. 46, 9584 (2007)

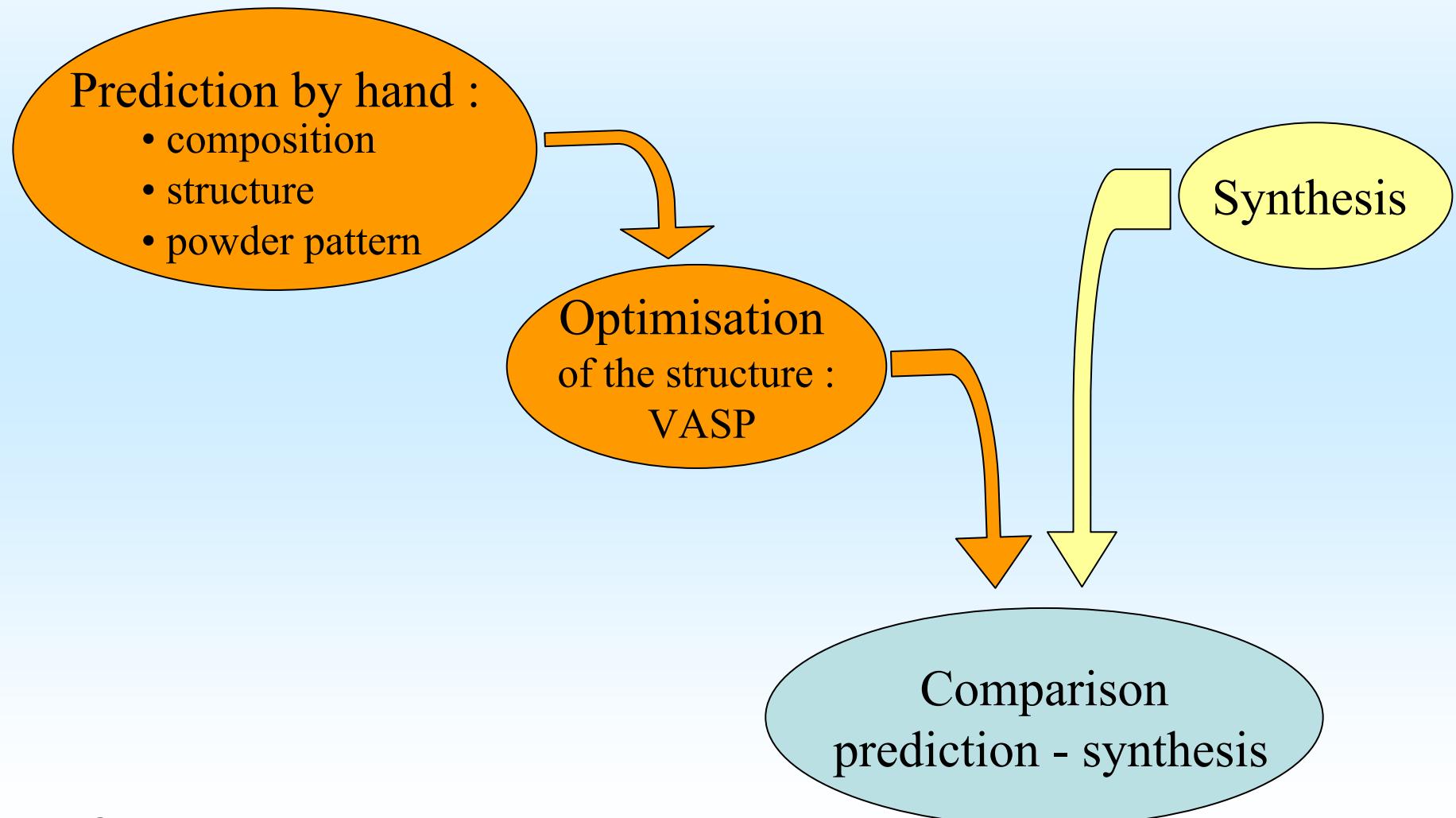
Concevoir un nouveau composé à structure composite lamellaire : un lego chimique ?



- layers = secondary building units
- Similar in-plane parameters
- Electronic transfer
- Redox competition between cations

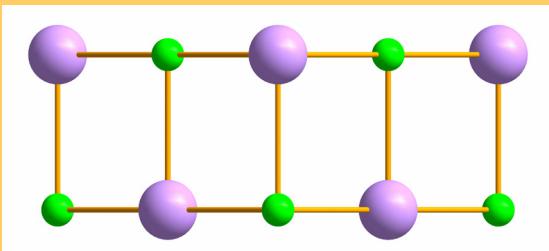


Concevoir un nouveau composé à structure composite lamellaire : un lego chimique ?

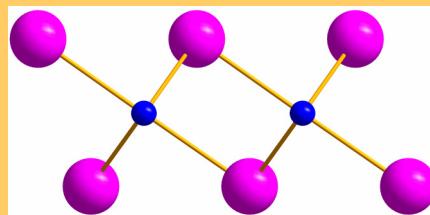




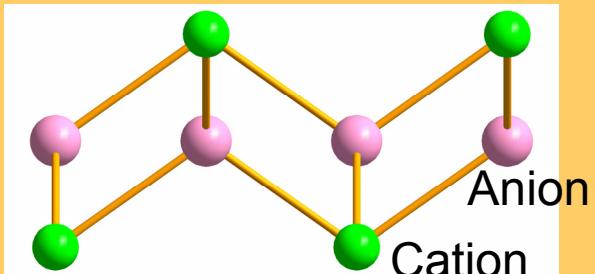
NaCl



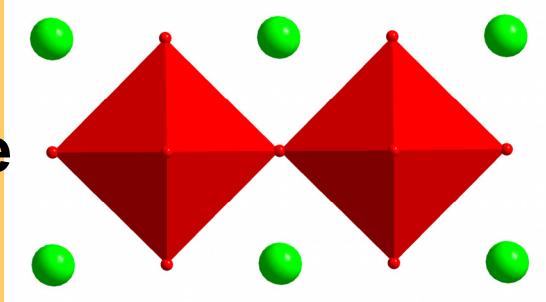
CdI₂



Fluorine

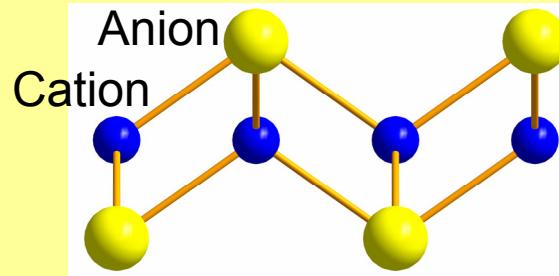
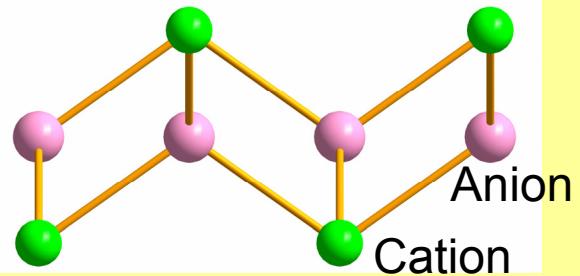


Pérovskite



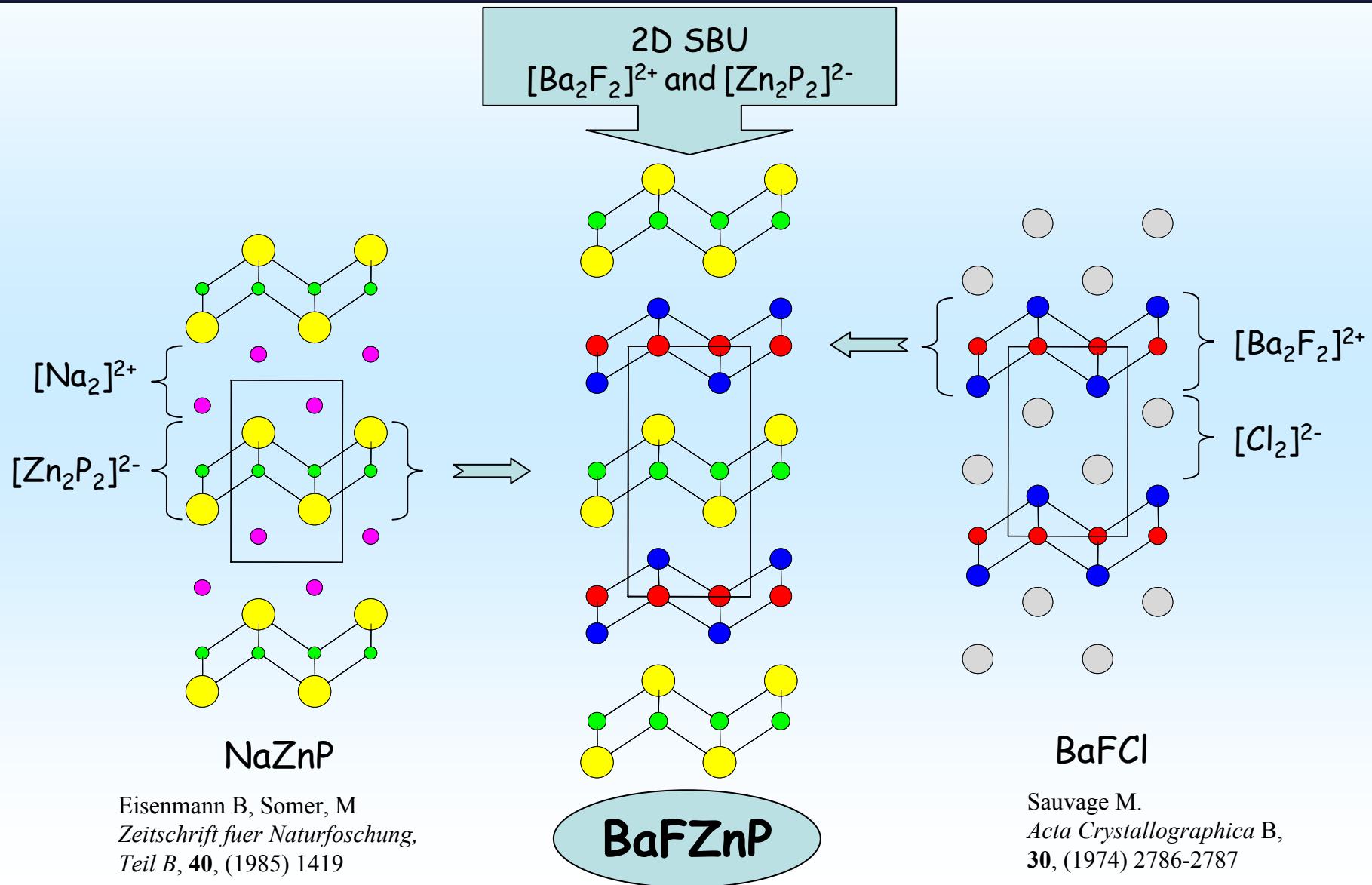


Fluorine

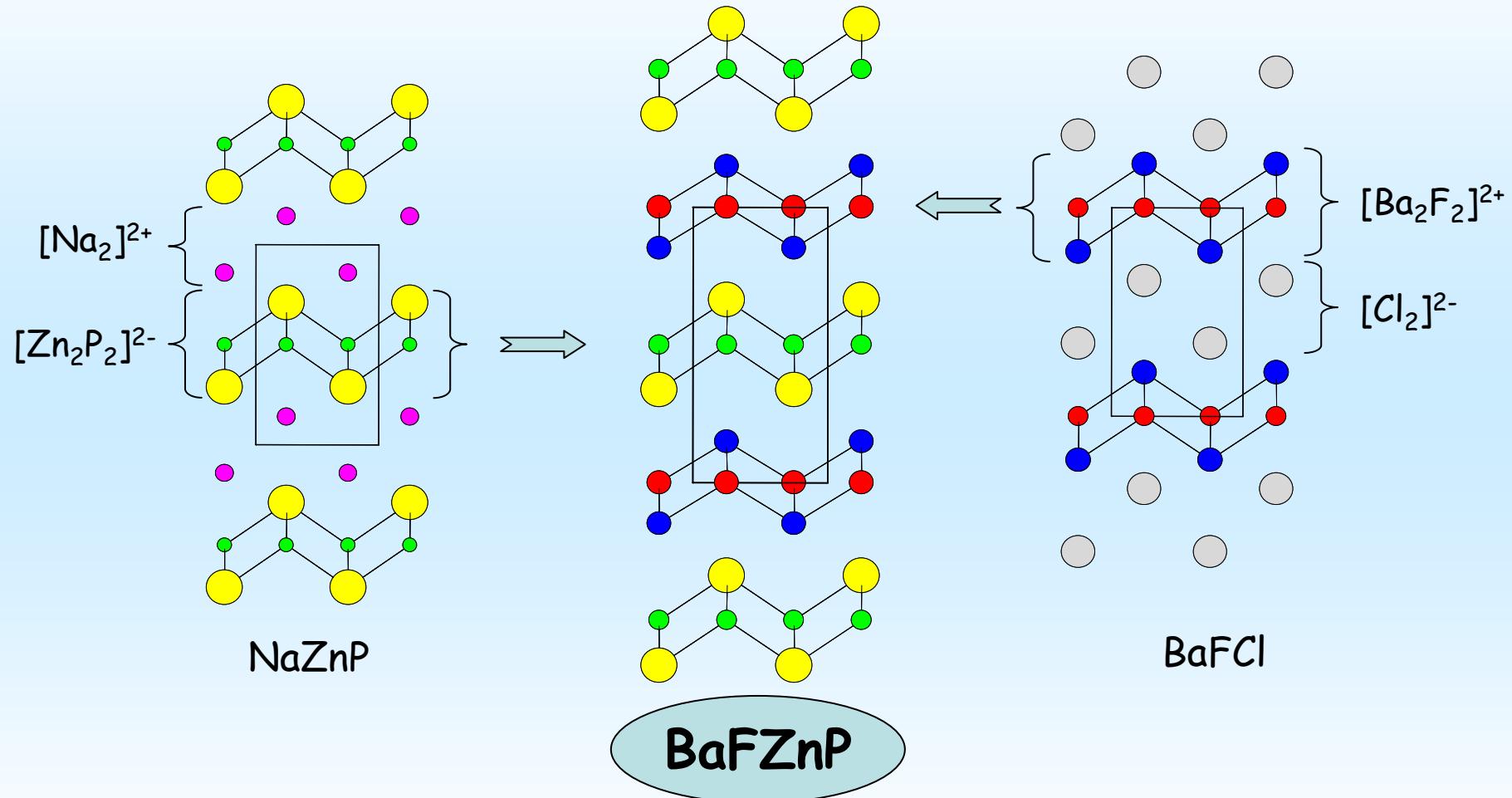


**Anti-
Fluorine**

Application aux blocs fluorines et antifluorines



Application aux blocs fluorines et antifluorines



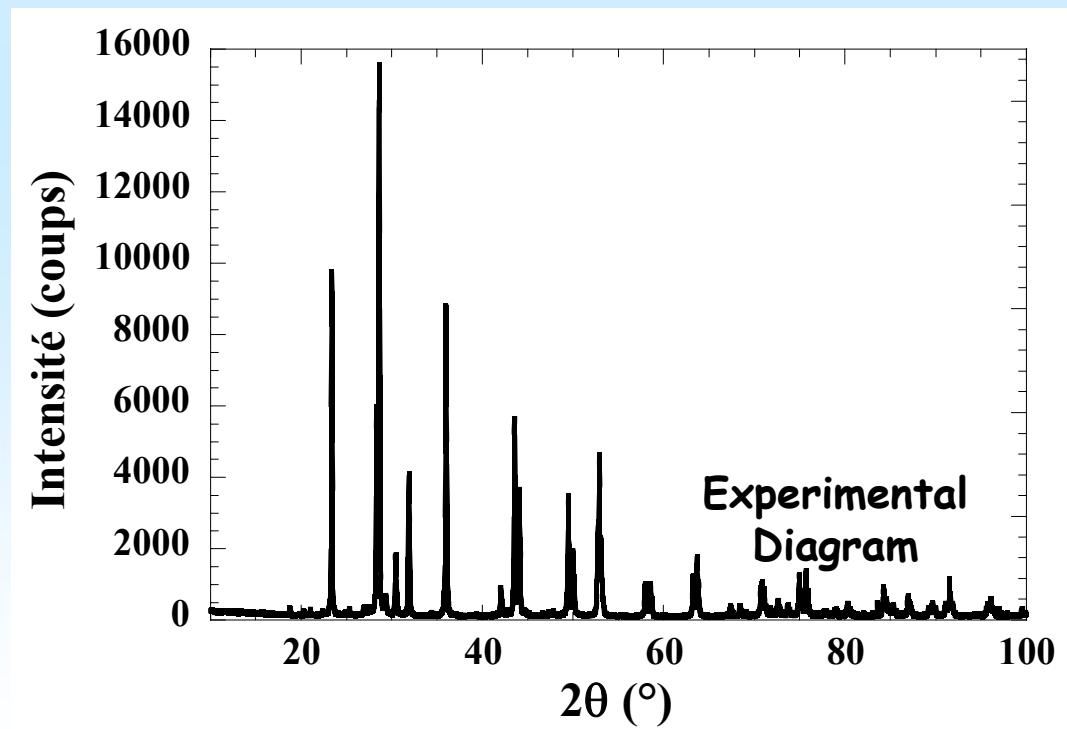
$$\Delta_r G = -26,0 \text{ kJ.mol}^{-1}$$

Optimized structure
with VASP

Synthèse du composé BaFZnP

Synthesis

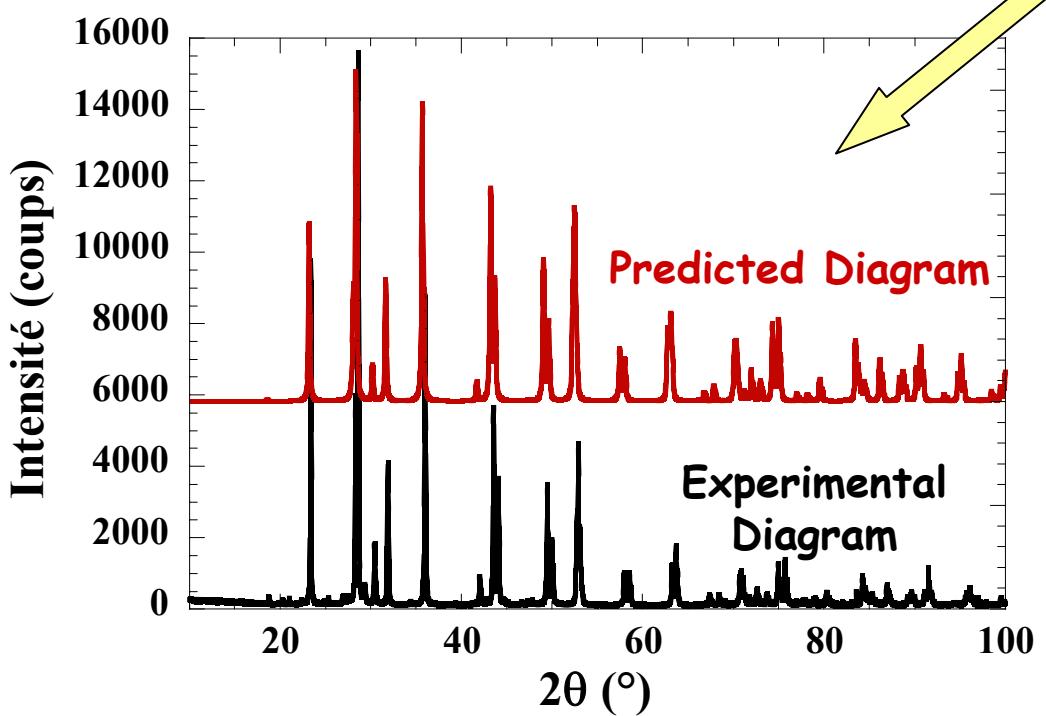
- Metathesis (600 °C) → NaCl + new phase
- HT ceramic (900 °C) → new phase



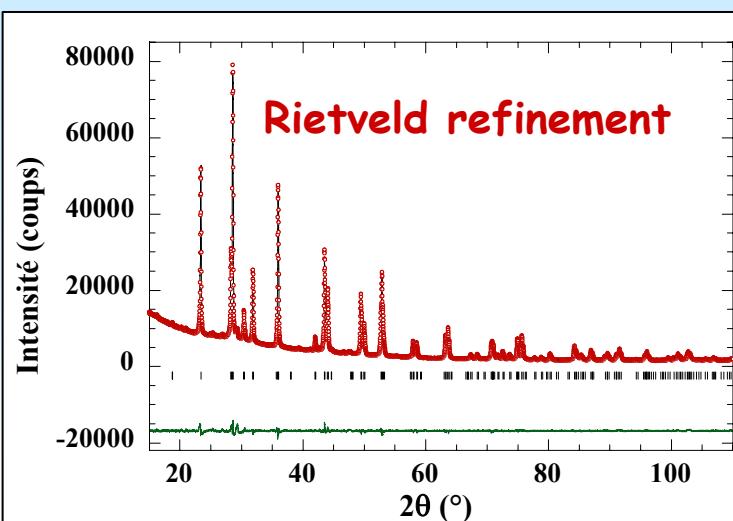
Affinement structural du composé BaFZnP

Optimised (VASP)
I4/nmm
 $a=4.1625\text{\AA}$ $\neq (0.2\%)$
 $c=9.4842\text{\AA}$ $\neq (0.3\%)$

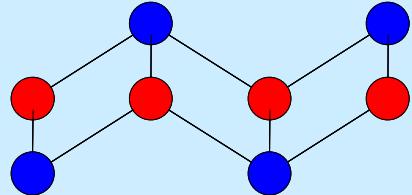
Predicted Structure



Refined structure
I4/nmm
 $a=4.1564(1)\text{\AA}$
 $c=9.4574(1)\text{\AA}$



$$R_{\text{Bragg}} = 2,05 \%$$



Ae₂F₂
Ae = Sr, Ba

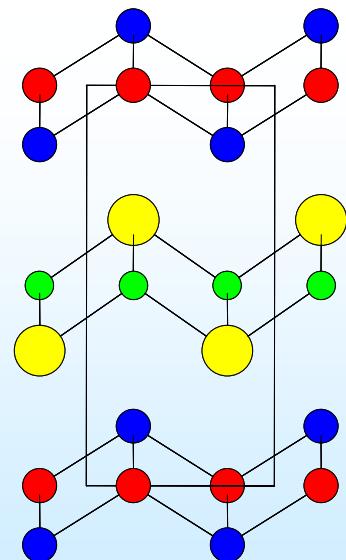
L. Cario; H. Kabbour
and A. Meerschaut
Chem. Mat. **17**, 234 (2005)

Ae₂F₂M₂P₂

(Ae = Ba, Sr; Pn = P,
Sb; M=Zn, Mn)

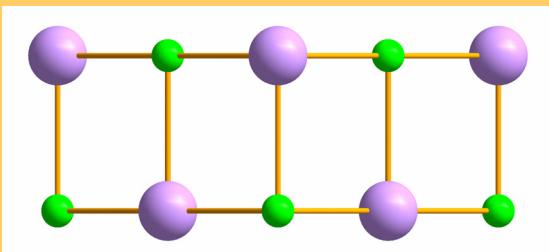
M₂Pn₂

H. Kabbour, L. Cario and F. Boucher,
J. Mater. Chem.
15, 3525 (2005).

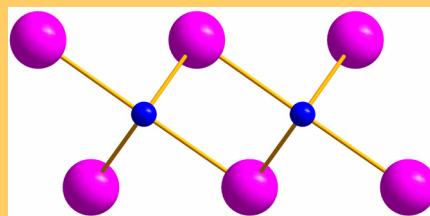




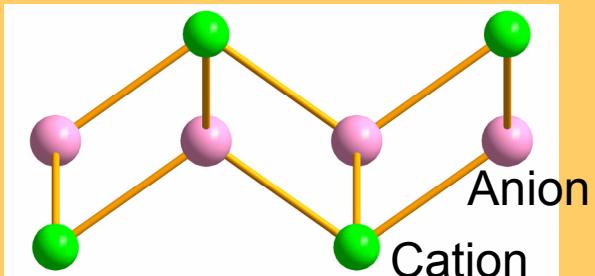
NaCl



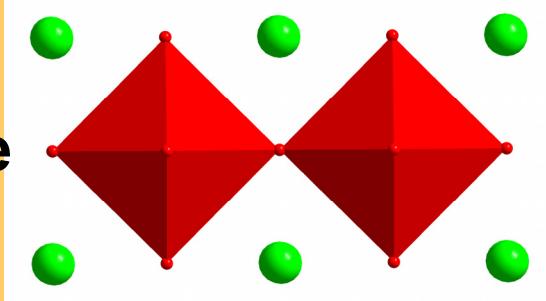
CdI₂



Fluorine

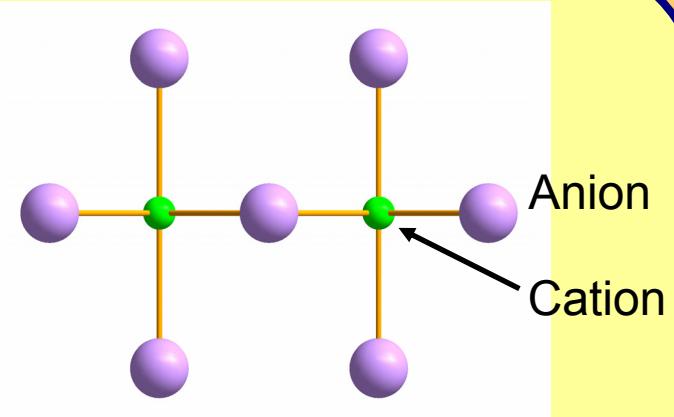


Pérovskite

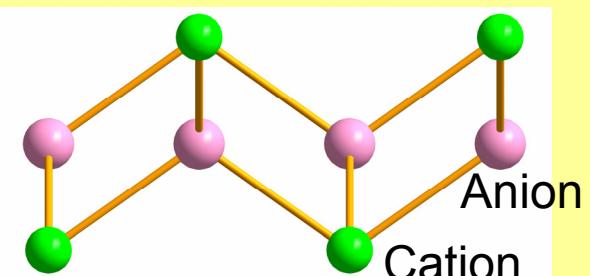




NaCl

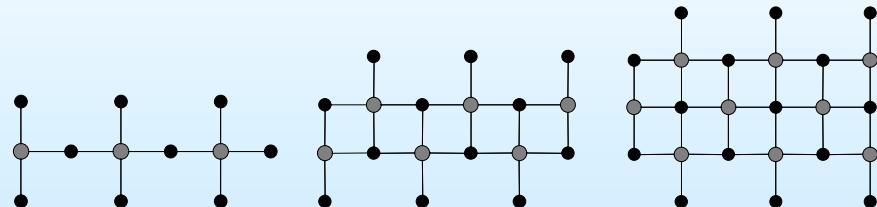


Fluorine



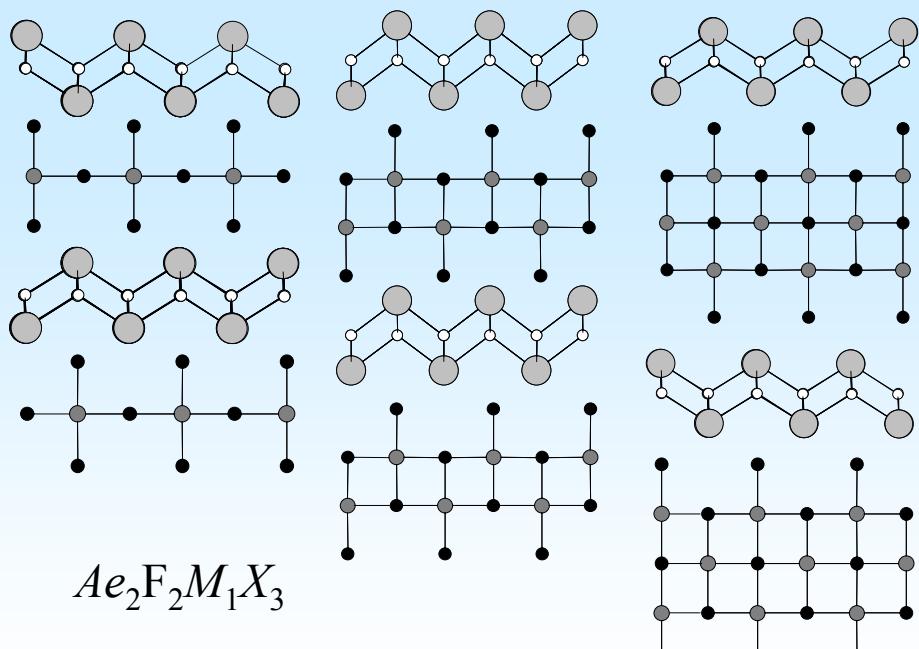
Application aux blocs fluorine et NaCl

Coupe (110) → blocs $^{(110)}\text{NaCl}$ → blocs à 3, 4 ou 5 couches d'anions



Associé au bloc
fluorine $[Ae_2F_2]$

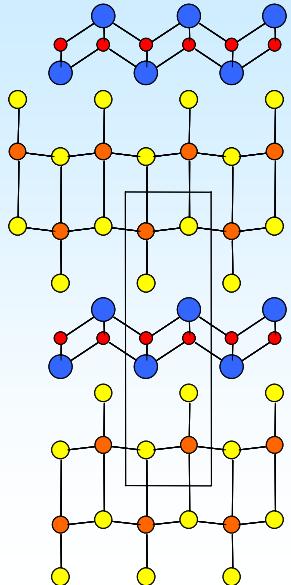
Série homologue $Ae_2F_2M_{1+n}X_{3+n}$



$Ae_2F_2M_1X_3$

$Ae_2F_2M_2X_4$

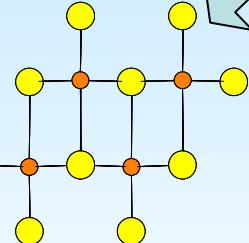
$Ae_2F_2M_3X_5$



Sr₂F₂Sb₂Se₄

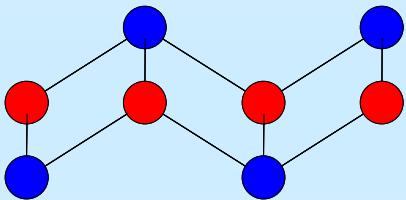
H. Kabbour, and L. Cario
Inorg. Chem. **45**, 2713 (2006).

Sb₂Se₄



Ae₂F₂
Ae = Sr, Ba

L. Cario; H. Kabbour
and A. Meerschaut
Chem. Mat. **17**, 234 (2005)



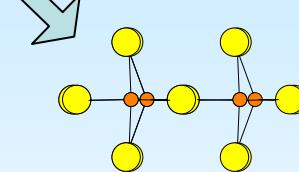
Ae₂F₂M₂P₂

(Ae = Ba, Sr; Pn = P,
Sb; M=Zn, Mn)

M₂Pn₂

H. Kabbour, L. Cario and F. Boucher,
J. Mater. Chem.
15, 3525 (2005).

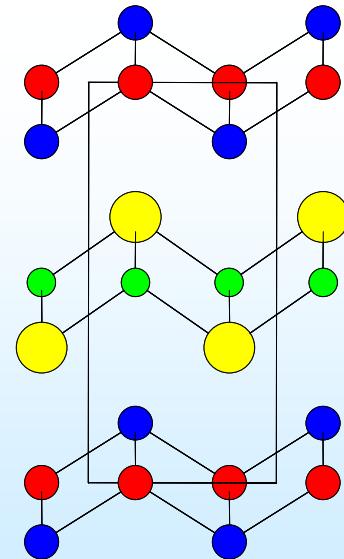
SnX₃



Ae₂F₂SnX₃

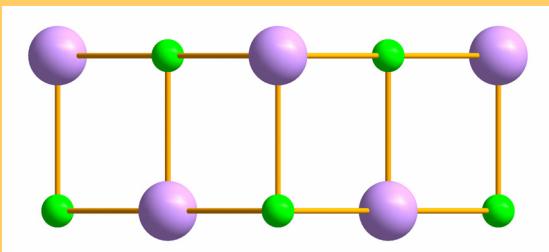
(Ae = Ba, Sr;
X = S, Se)

H. Kabbour, L. Cario, M. Danot
and A. Meerschaut
Inorg. Chem. **45**, 917 (2006).

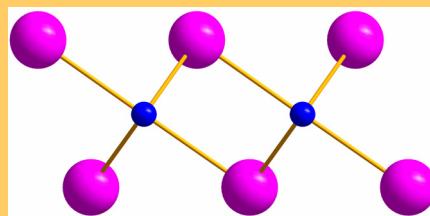




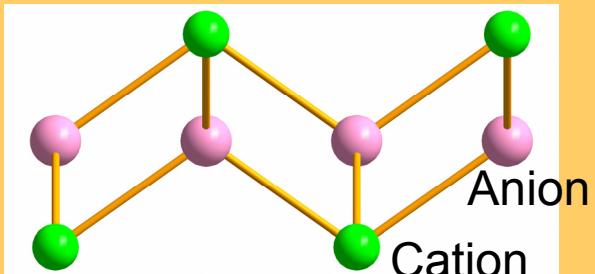
NaCl



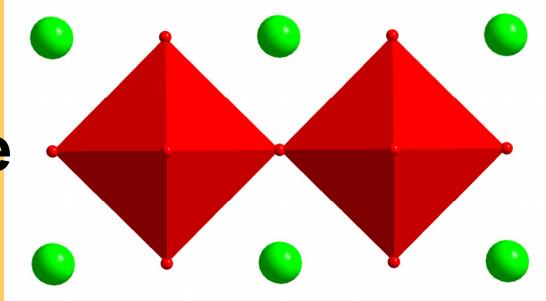
CdI₂



Fluorine

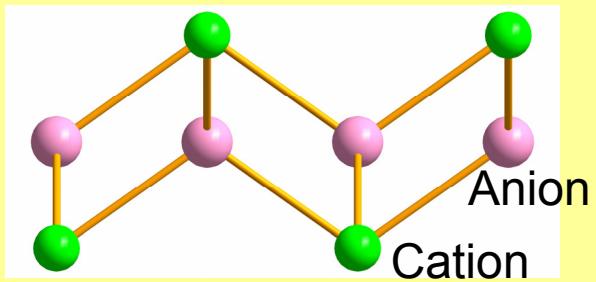


Pérovskite

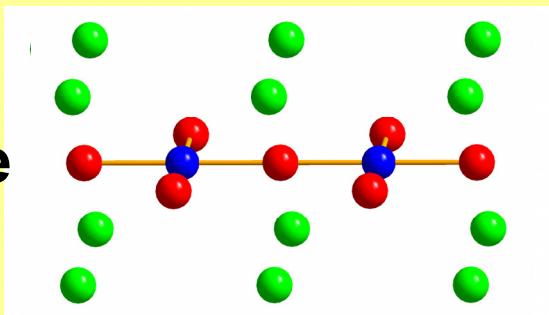




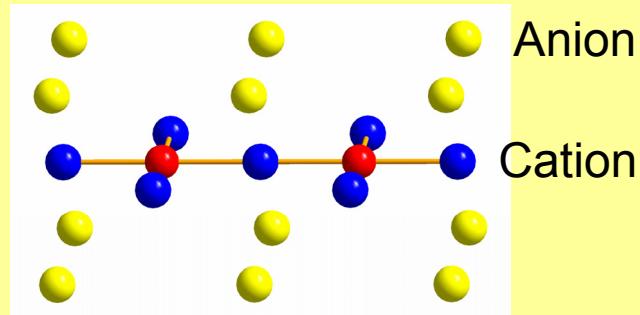
Fluorine



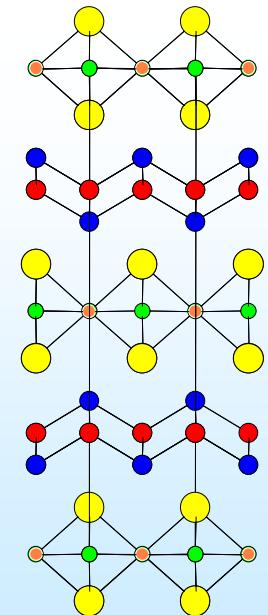
Pérovskite



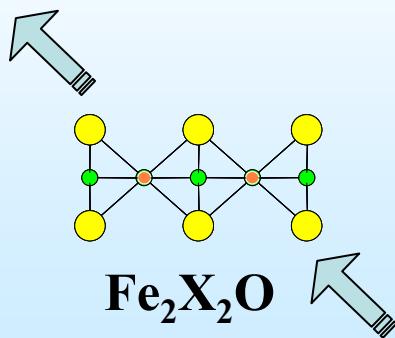
Plan CuO₂



Plan anti-CuO₂

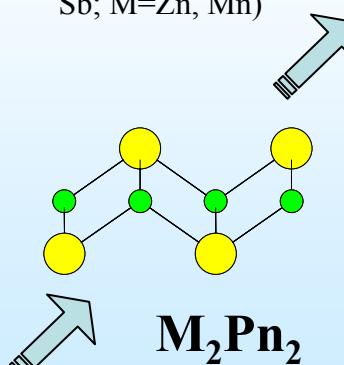


Ae₂F₂Fe₂X₂O
(Ae = Ba, Sr; X = S, Se)

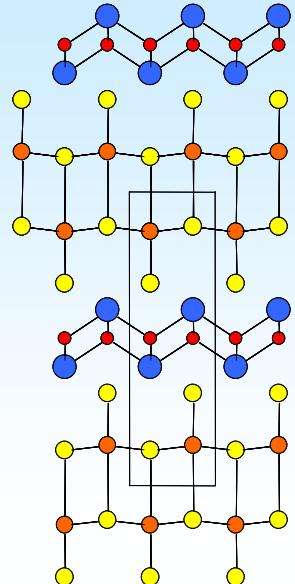


H. Kabbour et al.
J. Am. Chem. Soc. **130**, 8261 (2008)

Ae₂F₂M₂P₂
(Ae = Ba, Sr; Pn = P,
Sb; M=Zn, Mn)

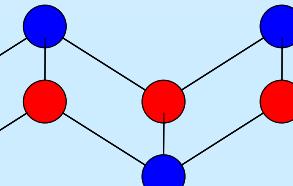


H. Kabbour, L. Cario and F. Boucher,
J. Mater. Chem. **15**, 3525 (2005).



Sr₂F₂Sb₂Se₄

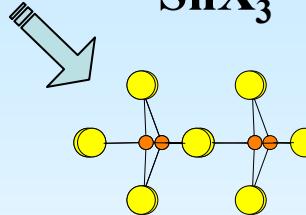
H. Kabbour, and L. Cario
Inorg. Chem. **45**, 2713 (2006).



Ae₂F₂
Ae = Sr, Ba

L. Cario; H. Kabbour
and A. Meerschaut
Chem. Mat. **17**, 234 (2005)

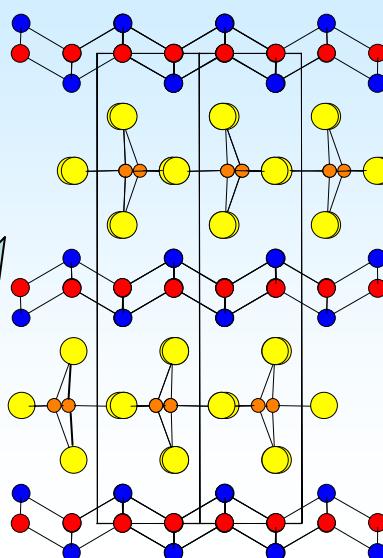
SnX₃



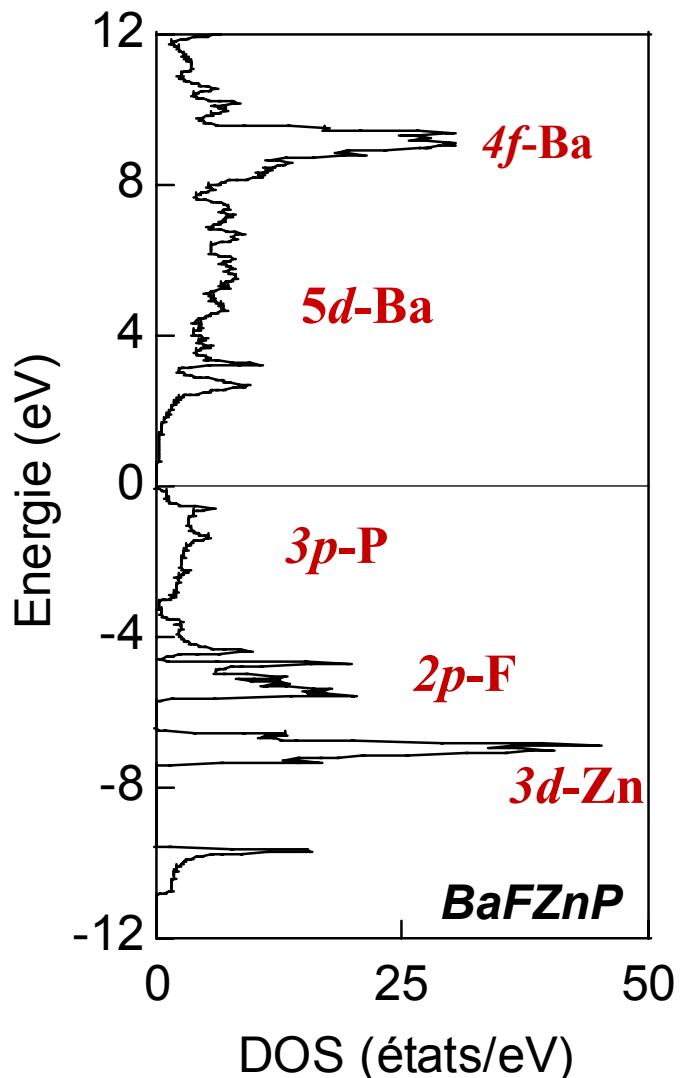
Ae₂F₂SnX₃

(Ae = Ba, Sr;
X = S, Se)

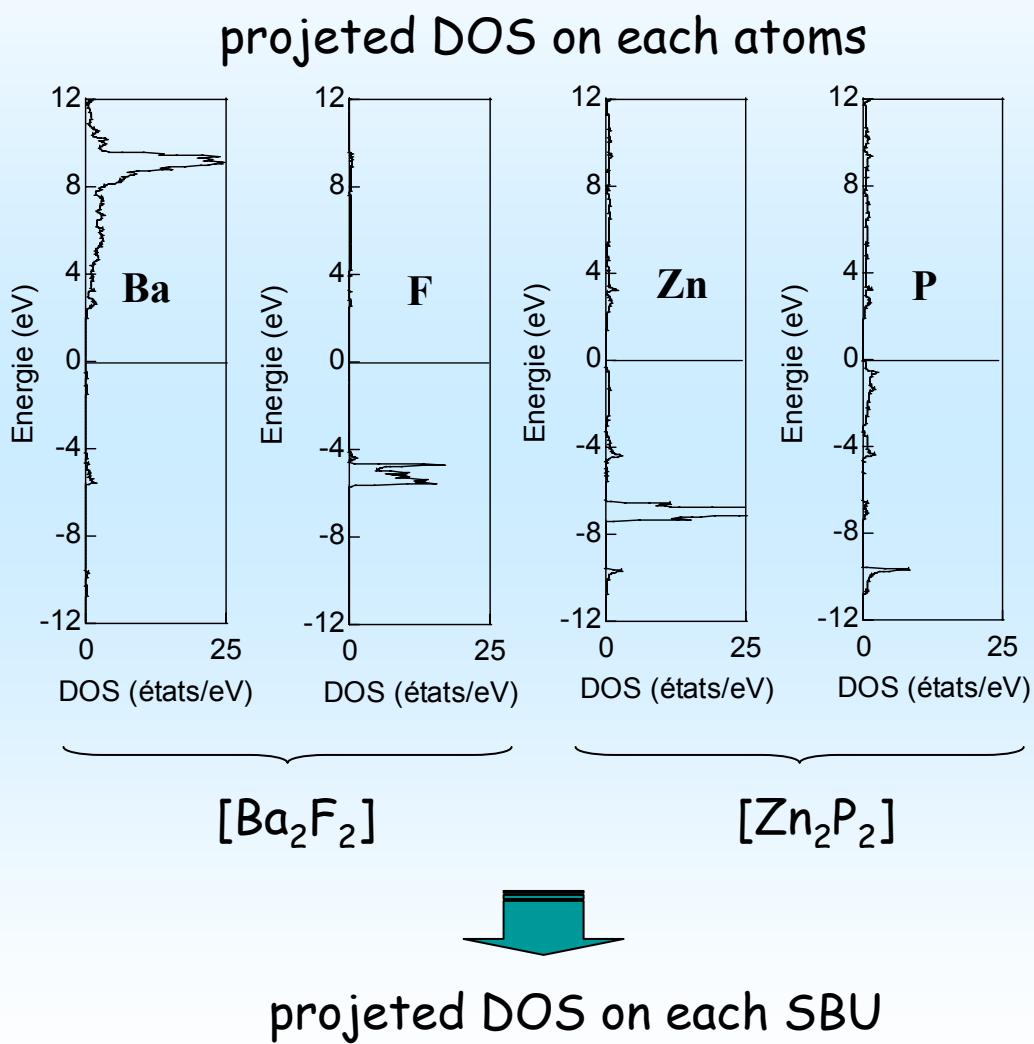
H. Kabbour, L. Cario, M. Danot
and A. Meerschaut
Inorg. Chem. **45**, 917 (2006).



Stabilité des SBU 2D : calculs de structure de bandes

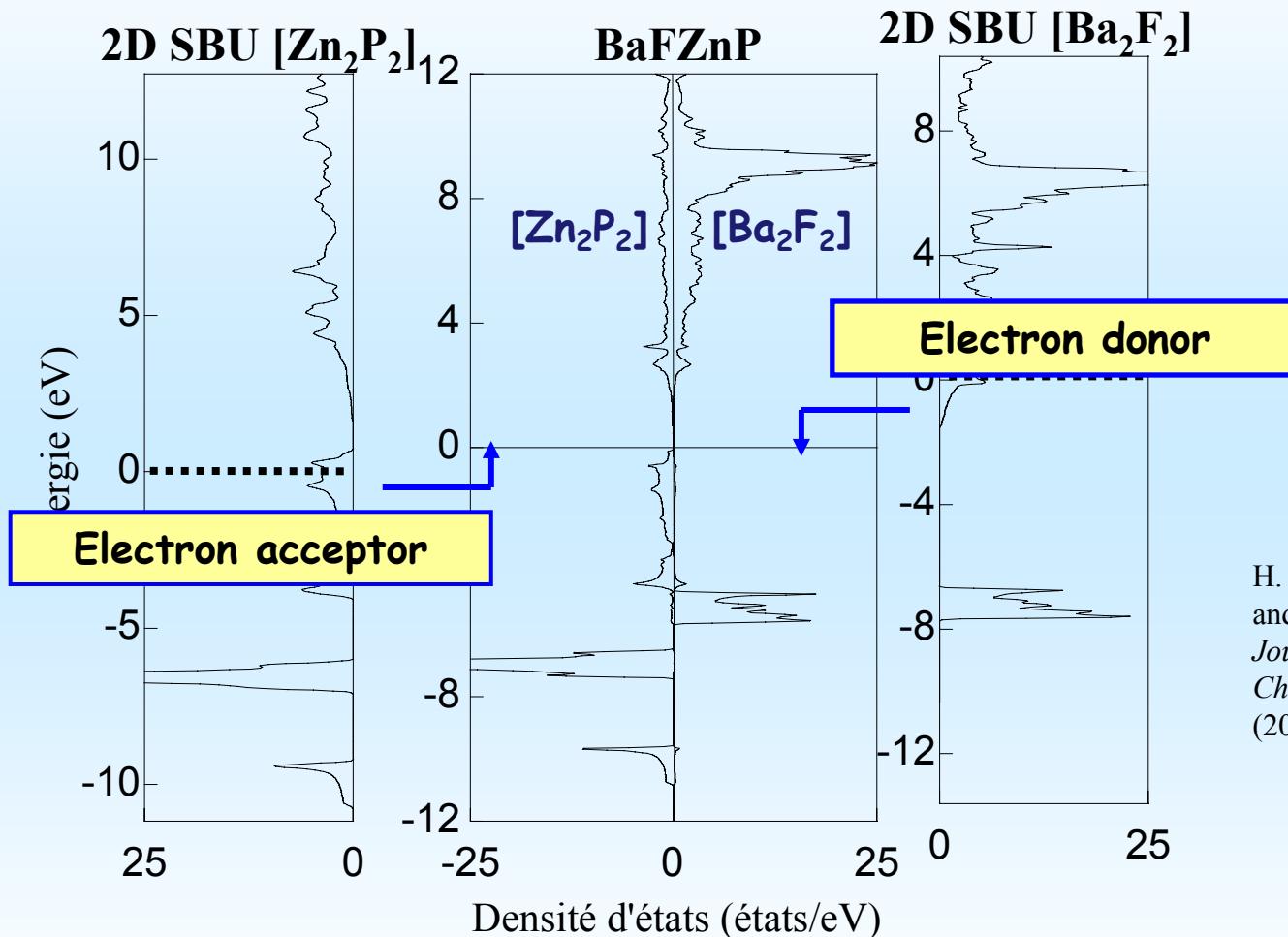


Wien2k calculations



H. Kabbour, L. Cario and F. Boucher,
Journal of Material Chemistry, **15**, 3525 (2005).

Stabilité des SBU 2D : calculs de structure de bandes



H. Kabbour, L. Cario
and F. Boucher,
Journal of Material Chemistry, **15**, 3525
(2005).

2D SBU when assembled together could keep not only their structural features, but also their electronic structures.

Stabilité des SBU 2D : calculs de structure de bandes

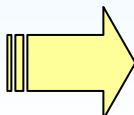
DOS of the SBU are weakly affected by each others



2D Secondary Building Units = Secondary Electronic Units



Stability of the SBU
Enable their
Assembly

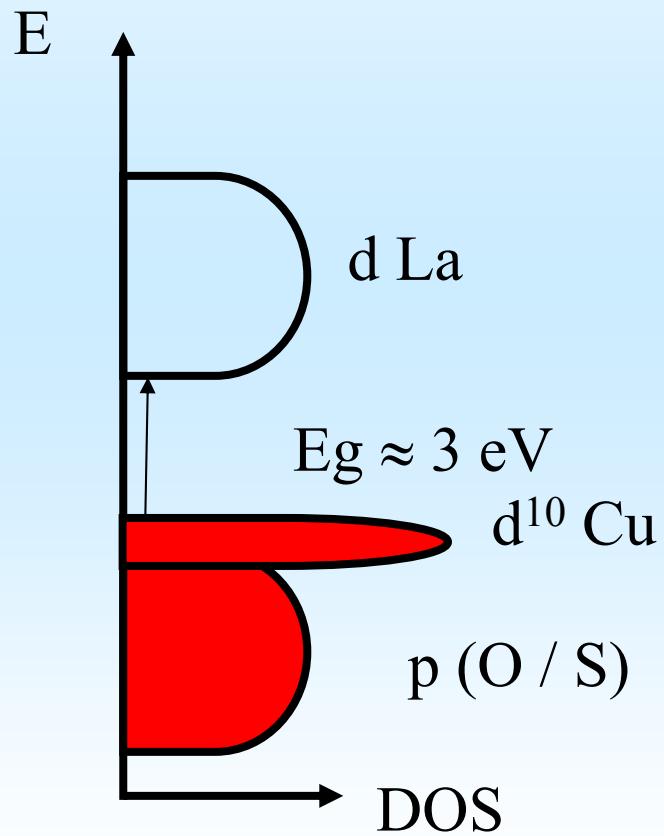
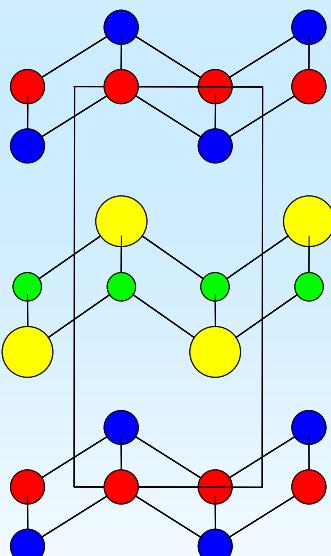
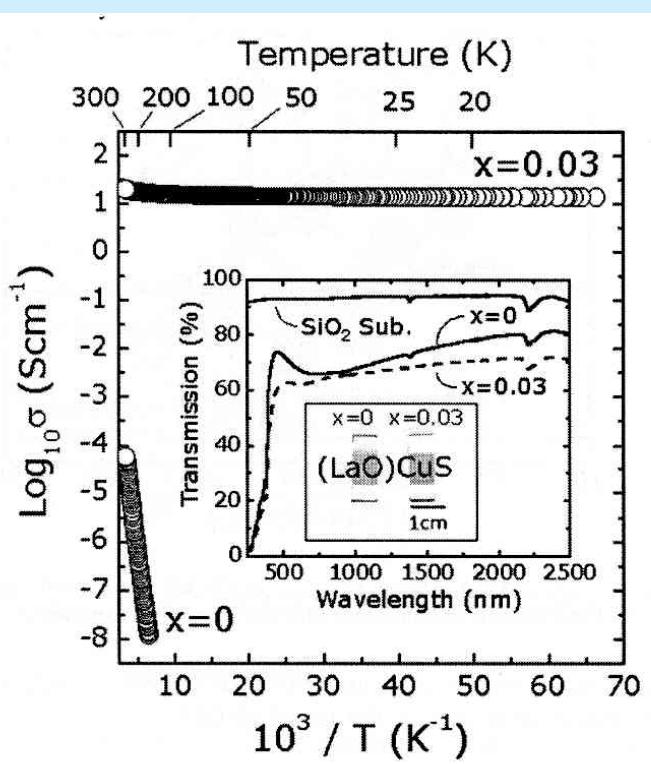


Do 2D SBU keep their properties ?
Can we design compounds with targeted properties ?

Conception d'un nouveau conducteur transparent de type p

- p-type Transparent Conductors : LnCuOS
gap $\approx 3 \text{ eV}$; $\sigma \approx 10 \text{ S.cm}^{-1}$

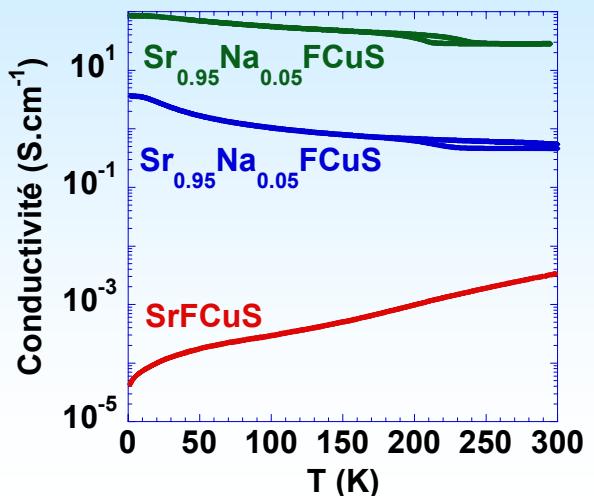
Hiramatsu et al. *Thin solid films* 411, 125-128 (2002)



D'après Inoue et al., *Phys. Rev. B* 64, 254211 (2001)

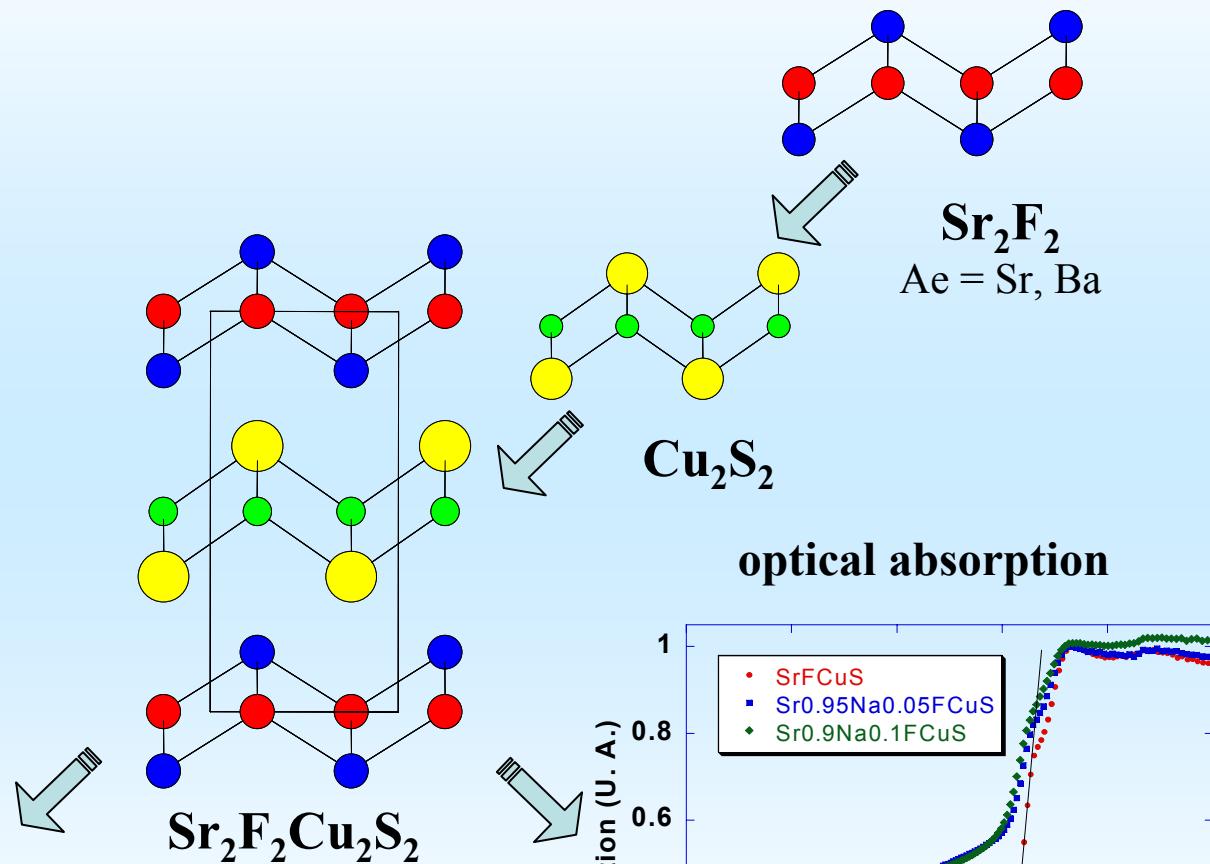
SrFCuS : nouveau conducteur transparent de type p

Electrical Conductivity

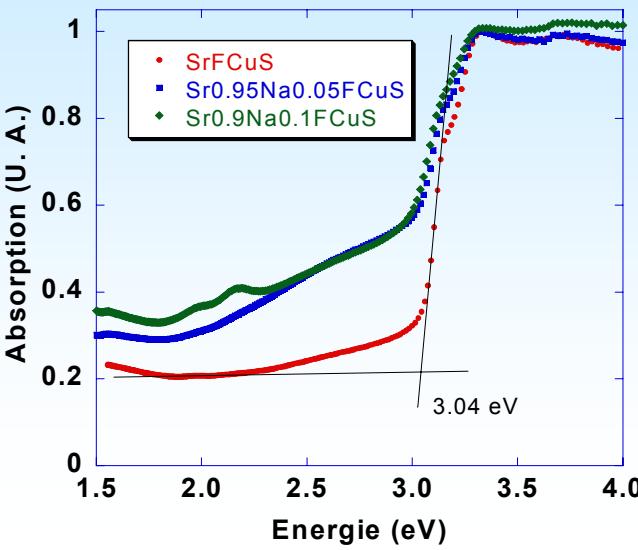


Nouveau Conducteur Transparent de type p

H. Kabbour, L. Cario, S. Jobic and B. Corraze,
J. Mater. Chem. **16**, 4165 (2006)



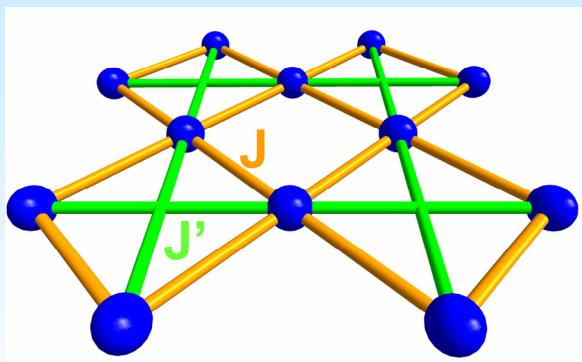
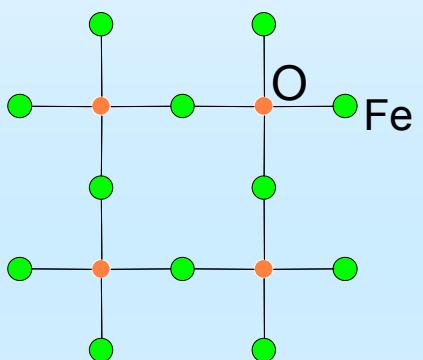
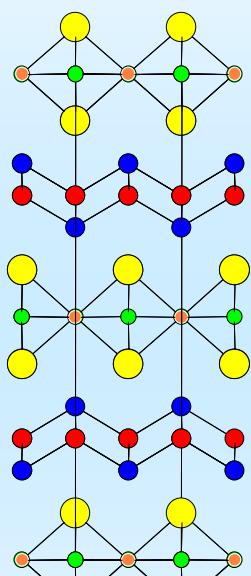
optical absorption



3.04 eV

Conception d'un nouveau composé à plans anti CuO_2

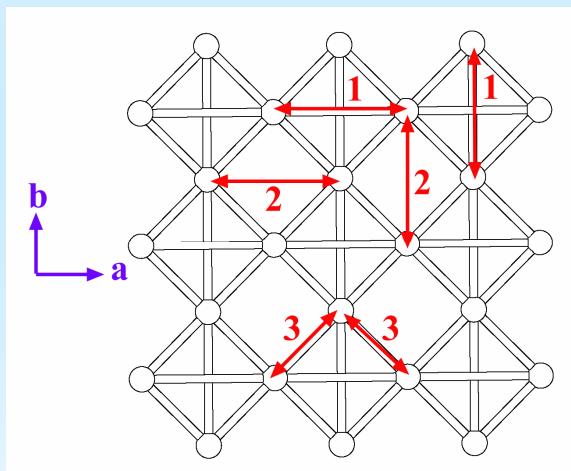
Plan Fe_2O type anti- CuO_2



Un rare exemple
de réseau checkerboard antiferromagnétique frustré

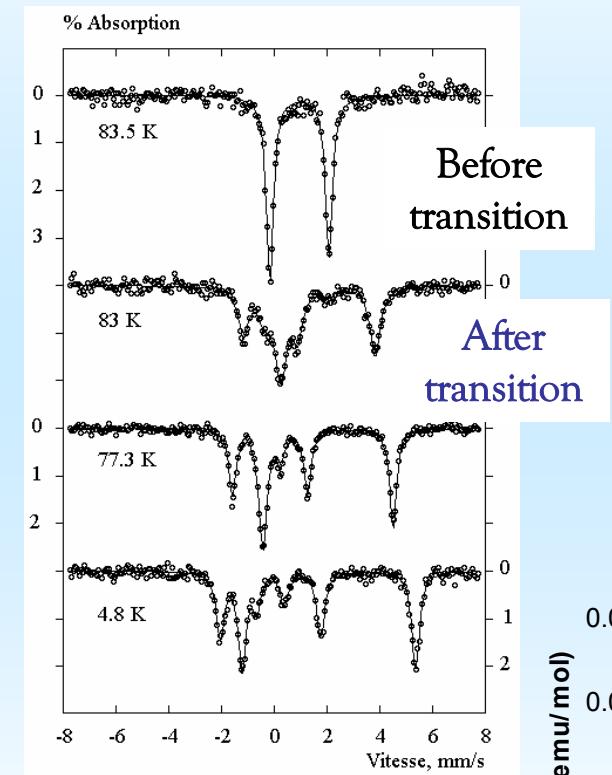
GGA+U calculations M. Whangbo

U (eV)	J_1 (meV)	J_2 (meV)	J_3 (meV)
4.5	-2.8	+0.9	-2.3

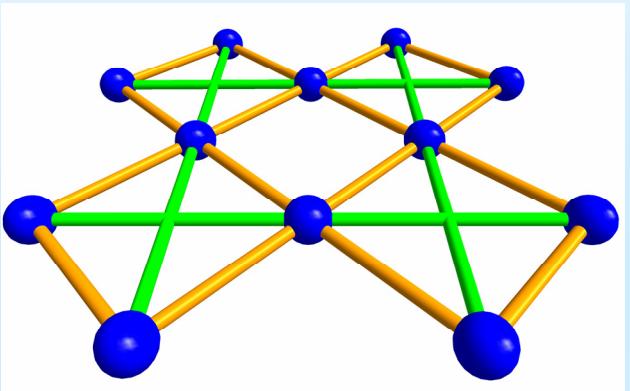


Conception d'un nouveau composé à plans anti CuO₂

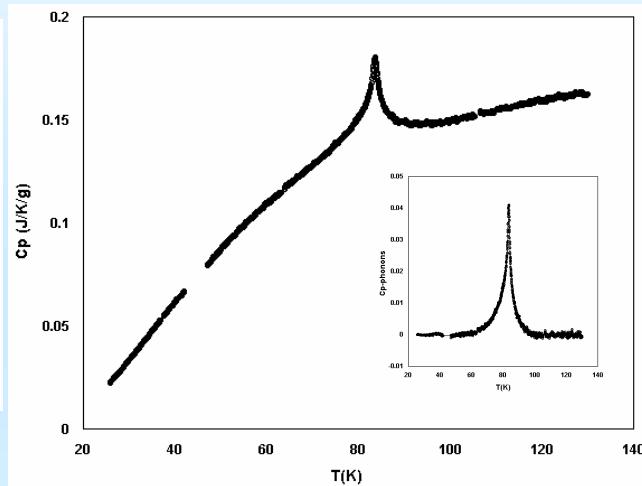
Mössbauer Study



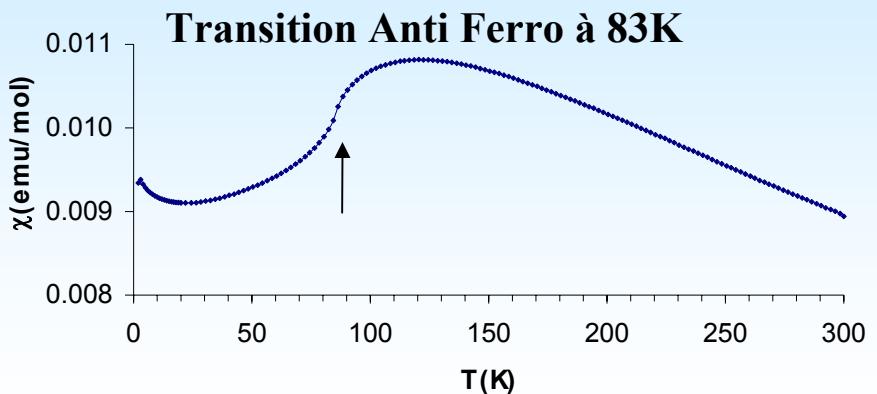
Ba₂F₂Fe₂Se₂O



Specific Heat



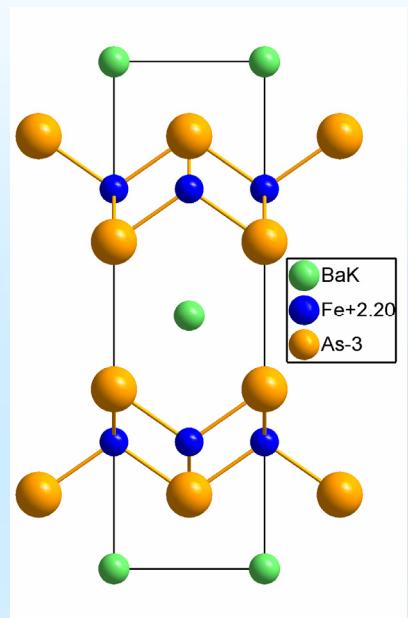
Magnetic Susceptibility



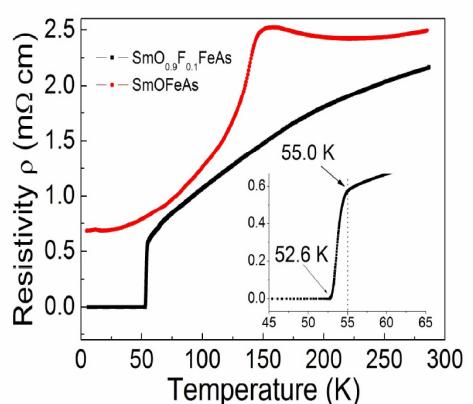
Théorie. $J'/J > 0.75$:
transition Néel →
état "non-conventionnel",
non-magnétique
B. Canals,
PRB 65, 184408 (2002)

Notre réseau checkerboard s'ordonne à basse température ...

Supraconductivité dans les FeAs



$\text{BaFe}_2\text{As}_2 \text{Tc} = 38 \text{ K}$
Jorhendt et al. 2008



2006: $\text{LaFePO} \text{Tc} = 3.2 \text{ K}$



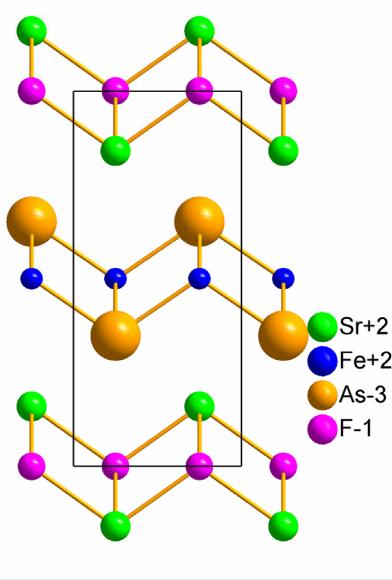
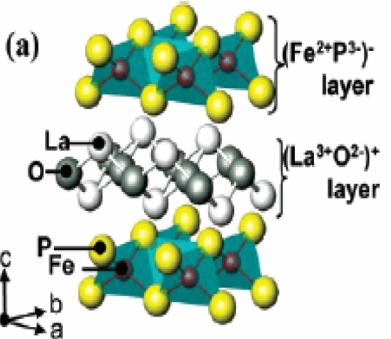
Published on Web 07/15/2006

Iron-Based Layered Superconductor: LaOFeP

Yoichi Kamihara,¹ Hidenori Hiramatsu,¹ Masahiro Hirano,^{1,‡} Ryuto Kawamura,[§] Hiroshi Yanagi,[§] Toshio Kamiya,^{†,§} and Hideo Hosono^{*†,‡}

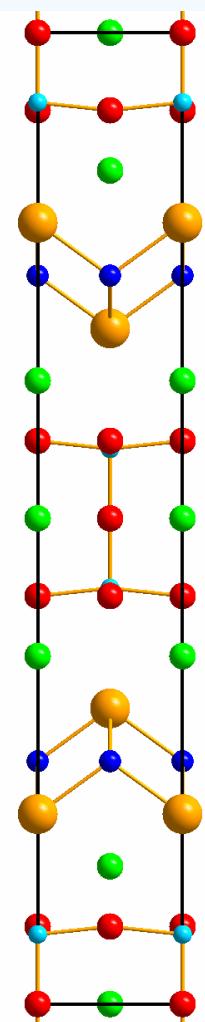
ERATO-SORST, JST, Frontier Collaborative Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, Frontier Collaborative Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and Materials and Structure Laboratory, Tokyo Institute of Technology, Mail Box R3-4, 4259 Nagatsuta, Yokohama 226-8503, Japan

Received May 15, 2006; E-mail: hosono@msl.titech.ac.jp



SrFeAs supra
Hosono et al. 2008

2008: Supraconductivité à $\text{Tc} = 26 \text{ K}$ dans $\text{LaFeAs(O}_{1-x}\text{F}_x\text{)}$
Groupe d'Hosono, J. Am. Chem. Soc. 130.



$\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$
Zhu et al. 2008

2008 : Superconductivity at 55K in $\text{Sm}[O}_{1-x}\text{F}_x\text{]FeAs}$
Groupe de Zhao Zhong-Xian Chinese Physics Letters

Conclusion

- *Il est difficile de prédire les structures stables des matériaux inorganiques*
- *Il est possible de jouer avec les empilements déjà connus pour concevoir des composés de manière raisonnée*
- *Les relations structures-propriétés dans des empilements connus permettent de cibler des propriétés dans de nouveaux composés contenant ces empilements*
- *Par contre il reste difficile de prédire les propriétés de nouveaux empilements !*